**T.R.**
**SAKARYA UNIVERSITY**
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

# PREPARATION OF POLYBENZOXAZINE-EPDM RUBBER BASED HYDROPHOBIC NANOCOMPOSITE MATERIALS

**MSc THESIS**

**Ebru KURTARAN**

**Nanoscience and Nanoengineering Department**

**AUGUST 2023**

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**Thesis Co-Advisor: Prof. Dr. Uğursoy OLGUN**

**AUGUST 2023**

The thesis work titled "PREPARATION OF POLYBENZOXAZINE-EPDM RUBBER BASED HYDROPHOBIC NANOCOMPOSITE MATERIALS" prepared by Ebru KURTARAN was accepted by the following jury on 08/08 /2023 by unanimously/majority of votes as a MSc THESIS in Sakarya University Graduate School of Natural and Applied Sciences, Nanoscience and Nanoenginnering department,

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(signature)

Ebru KURTARAN

*To my husband and lovely family*

## ACKNOWLEDGMENTS

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# ABBREVIATIONS

| | | |
|---|---|---|
| **ALA** | : Amino lauric acid |
| **ATBAN** | : Amine terminated polybutadiene co acrylonitrile |
| **Azo-COOH** | : 4-(4- hydroxyphenylazo) benzoic acid |
| **BZ** | : Benzoxazine |
| **BF3-MEA** | : Boron trifluoride monoethylamine |
| **DBA** | : Diallyl bisphenol A |
| **DGEBA** | : Diglycidyl ether |
| **DMA** | : Dynamic mechanic analysis |
| **DMAE** | : Dimethyle amino ethanol |
| **DMS** | : Dimethyle stearyl amine |
| **DSC** | : Differential scanning calorimetry |
| **EPDM** | : Ethylene propylene diene monomer |
| **FTIR** | : Fourier-Transform Infrared Spectroscopy |
| **GF** | : Glass fiber |
| **Gly-Si** | : Diglycidyloxymethylphenylesilan**e** |
| **HTBD** | : Hydroxyle terminated polybutadiene co acrylonitrile |
| **HRC** | : Heat release capacity |
| **LOI** | : Limiting oxygen index |
| **LOX** | : Liquid oxygen tank |
| **MMT** | : Montmorillonite |
| **NBR** | : Nitrile butadiene rubber |
| **OMMT** | : Organically modified montmorillonite |
| **PANI** | : Polyaniline |
| **PANI ES** | : Polyaniline emeraldine salt |
| **PBZ** | : Polybenxozazine |
| **PC** | : Polycarbonate |
| **PCL** | : Polycaprolactone |
| **PEO** | : Polyethylenokside |
| **POSS** | : Polyhedral oligomeric silsesquioxane |
| **PP** | : Polypropylene |

| | |
|---|---|
| **PTSA** | : P-toluene sulfonic acid |
| **PU** | : Polyurethane |
| **Py-NH2** | : Paraformaldehyde and aminopyrine |
| **ROP** | : Ring opening polymerization |
| **SBR** | : Styrene butadiene rubber |
| **SiO$_2$** | : Silica |
| **TBMI** | : Trimethyl hexane maleimide |
| **PTFE** | : Polytetrafluoroethylene |
| **Tg** | : Glass transition temperature |
| **TGA** | : Thermal gravimetric analysis |
| **THR** | : Total heat release |
| **TiO$_2$** | : Titanium dioxide |
| **UV** | : Ultraviolet light |
| **WRHA** | : White rice hisk ash |
| **ZDMA** | : Zinc Di methacrylate |

:

## SYMBOLS

**nm**        : Nanometer

**μ**         : Dynamic Viscosity

**E**         : Modulus of Elasticity

**ε**         : Strain Tensor

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# PREPARATION OF POLYBENZOXAZINE-EPDM RUBBER BASED HYDROPHOBIC NANOCOMPOSITE MATERIALS

## SUMMARY

The aim of this thesis is to prepare a hydrophobic nanocomposite with Polybenzoxazine (PBZ) and ethylene-propylene-diene-monomer rubber (EPDM) filled by nano titanium dioxide ($TiO_2$) and polytetrafluoroethylene (PTFE/Teflon).

In this work, the first step in the process is to synthesize fluorine-containing PBZ. Fluorine is intended to contribute to hydrophobicity of the PBZ. PBZ was synthesized by ring-opening polymerization, catalyzed by dimethyl amino ethanol (DMAE) base catalyst using benzoxazine monomer obtained from 4-hydroxy benzaldehyde, 2-(trifluoromethyl)aniline and paraformaldehyde. In order for the PBZ polymer to be ring-opening polymerization to take place, the reactants were magnetically mixed in an oil bath at 100 °C for 24 hours. As a result of polymerization, a hard brittle, light-yellow color solid polymer was obtained.

Since the synthesized PBZ is a hard and brittle polymer on its own, it is necessary to get help from another polymer to improve the elasticity for polymer nanocomposite samples. Thus, it was prepared a blend with PBZ and EPDM rubber.

Polymer nanocomposite samples with weigh ratios of 40% EPDM and 40% PBZ blend matrix, 10% nano $TiO_2$ and 10% PTFE additives were prepared. Since at least one of the fillers must be nano-sized in order to meet the condition of being a nanocomposite, 0-20 nanometer $TiO_2$ additive is used. Both nano $TiO_2$ and PTFE additives helped to prepare a hydrophobic polymer nanocomposite.

Since one of the matrix components is EPDM rubber, some of the samples were cross-linked with 0.1% sulfur by weight to perform the vulcanization step, which is an important step in the use of rubber material. Polymer nanocomposite samples prepared with and without sulfur were heated and cured with temperatures of 25 °C, 100 °C, 150 °C and 180 °C, respectively.

The effect of sulfur and curing temperature on the hydrophobicity of polymer nanocomposite samples was studied. The EPDM-PBZ nanocomposites were also characterized by UV-vis., TGA-DTA, SEM, SEM-EDX, FTIR, contact angle measurement characterizations.

The contact angle was noted as 101.1° for PBZE1-EPDM-PTFE-Nano $TiO_2$ nanocomposite sample. According to the UV results, the samples showed wide range abroad absorption peaks.

According to all test results, the preparation of a hydrophobic polymer nanocomposite was successful. It was observed that the additives were homogeneously distributed in the matrix, there was no agglomeration. When the prepared polymer nanocomposites were compared to whether they were hydrophobic or not, it was clearly seen that the temperature and the curing process by cross-linking with sulfur increased the hydrophobicity in the samples. In particular, the EPDM-PBZ polymer nanocomposite

sample with sulfur, vulcanized at 150 °C presented better hydrophobic features with a contact angle of 110°.

# POLİBENZOKZAZİN-EPDM KAUÇUK ESASLI HİDROFOBİK NANOKOMOZİT MALZEMELERİN HAZIRLANMASI

## ÖZET

Bu tez çalışmasının amacı, Polibenzoksazin (PBZ) ve etilen-propilen-dien-monomer kauçuk (EPDM) polimer blend matrisi ile, nano titanyum dioksit (TiO₂) ve politetrafloroetilen (PTFE/Teflon) katkılı hidrofobik polimer nanokompozit numuneleri hazırlamaktır.

Polimer nanokompozit hazırlamak için bileşen olarak polimer bir matris ve en az bir adet nano boyutta katkı kullanmak gerekir. Katkı veya dolgu malzemenin matris içerisinde homojen dağılması, topaklanma olmaması, polimer nanokompozitin başarılı bir şekilde hazırlanması için gereklidir. Hidrofobik bir polimer nanokompozit hazırlamak için bileşenler hidrofobik olmalıdır. Bu çalışmada da bütün bileşenlerin hidrofobik olması ve/veya hidrofobik yüzey özelliklerine katkı sağlaması amaçlanmış ve uygulanmıştır.

PBZ kürlenebilen fenolik bir reçine sistemidir. Epoksi gibi polimer kompozit üretiminde sık kullanılan fenolik reçinelerle kıyaslandığında birçok avantajıyla yeni bir perspektif oluştururlar. PBZ kimyasal olarak amin, fenol ve formaldehitten sentezlenir. Birçok farklı benzokzazin monomeri ile sentezlenebilmesi, PBZ polimeri için geniş uygulama alanlarında kullanımına olanak sağlamıştır. Geniş uygulama alanı yanında iyi mekanik mukavemet, alev geciktirme, boyutsal kararlılık, çeşitli çözücülere karşı direnç, sıfıra yakın hacimsel değişim, kürleme için güçlü asit katalizörü gerektirmemesi, kürleme sıcaklığından çok daha yüksek camsı geçiş sıcaklığı, düşük su emilimi, PBZ polimerlerinin en önemli avantajlarındandır. Uygulamada farklı benzokzazin monomerlerinden sentezlenen PBZ ile istenilen özellik polimere eklenebilir veya polimerin bir özelliği desteklenebilir.

Bu tez çalışmasında prosesteki ilk adım Flor katkılı PBZ sentezlemektir. Florun hidrofobikliğe katkı sağlaması amaçlanmıştır. PBZ, 4-hidroksi benzaldehit, 2-(triflorometil) anilin ve paraformaldehit monomerleri ile dimetil amino etanol (DMAE) bazı katalizörlüğünde, halka açılma polimerizasyonu ile sentezlenmiştir. PBZ polimeri, halka açılma polimerizasyonunun gerçekleşebilmesi için, reaktanlar yağ banyosu içerisinde 100 °C' de 24 saat boyunca manyetik olarak karıştırılmıştır. Polimerizasyon sonucunda açık sarı renkli sert kırılgan, katı bir polimer elde edilmiştir.

Sentezlenen PBZ tek başına sert ve kırılgan bir polimer olma özelliği gösterdiğinden, matris olarak kullanımının mümkün olması ve polimer nanokompozite elastikiyet kazandırmak için matris oluşturmada başka bir polimerden de yardım alınması gerekliliği ortaya çıkmıştır. Bunun için PBZ ile EPDM kauçuk blendi hazırlanmasına karar verilmiştir. EPDM elastikiyet özelliğinin yanı sıra oksidasyona, ısıya, hava koşullarına ve ozona karşı mükemmel direnç göstermesi gibi avantajlara sahiptir. Kimyasal olarak kararlı olması, yüksek plastikleştirici ve dolgu yüküne iyi yanıt vermeleri ve ucuz olmaları, kauçuk ve kompozit endüstrisinde tercih edilmelerini

sağlar. Elastikiyet ve sülfür ile çapraz bağlanabilme özellikleri hidrofobik bir polimer nanokompozit film hazırlamada PBZ' ye yardımcı olmuştur.

Ağırlıkça %40 EPDM ve %40 PBZ karışım matrisi ve %10 nano $TiO_2$, %10 PTFE katkıları ile polimer nanokompozit numuneler hazırlanmıştır. Nanokompozit olma şartını sağlayabilmesi için dolgulardan en az birinin nano boyutta olması gerektiğinden, bu şartı sağlayabilmesi için nano $TiO_2$ katkısı kullanılmıştır. Hem nano $TiO_2$ hem de PTFE katkıları hidrofobik bir polimer nanokompozit hazırlamaya yardımcı olmuştur.

Matris bileşenlerinden biri EPDM kauçuğu olduğundan, kauçuk malzemesi kullanımında önemli bir adım olan vulkanizasyon adımını gerçekleştirmek için numunelerin bir kısmı ağırlıkça %0,1 kükürt ile çapraz bağlanmıştır. Kükürtlü ve kükürtsüz olarak hazırlanan polimer nanokompozit numuneler sırasıyla 25 °C, 100 °C, 150 °C ve 180 °C sıcaklıklar ile ısıtılmış ve kürleme işlemi yapılmıştır.

Kükürt ve kürleme sıcaklığının polimer nanokompozit numunelerinin hidrofobikliğine etkisi, UV-vis., TGA-DTA, SEM, SEM-EDX, FTIR, temas açısı ölçümü karakterizasyonları ile gözlemlenmiştir.

Karakterizasyon sonuçlarına göre Ultraviyole (UV) mor ötesi görünür bölge spektroskopisi absorpsiyon piklerine bakıldığında, kükürtlü 150 °C 'de çapraz bağlanmış polimer nanokompozit numune daha geniş dalga boyunca daha yüksek derecede ışığı absorplamıştır. Genel olarak tüm numunelerin absorpsiyon değerleri incelendiğinde, yüksek sıcaklıkta çapraz bağlanmış polimer nanokompozit film numuneleri daha geniş absorpsiyon pikleri göstermiştir. Buna göre moleküllerin birbirleri ile iyi etkileşim gösterdiği sonucu çıkarılabilir.

SEM ve SEM-EDX görüntüleri, katkıların polimer nanokompozit filminde homojen olarak dağıldığını göstermiştir. Kayda değer bir aglomerasyon olmadığı görülmüştür. Bu durumun hidrofobikliğe katkısı sonuçlarda gözlemlenmiştir.

FTIR spektroskopisi ile hazırlanan numuneler ışığın infrared emilim yoğunluğuna karşı dalga sayısı 400–4000 $cm^{-1}$ aralığında ölçülmüştür. Bu karakterizasyon ölçümüne göre kükürt eklenmemiş 25 °C 'de kürlenmiş numune için yapılan FTIR ölçümünde 2920 $cm^{-1}$ ve 2851 $cm^{-1}$ 'de alifatik C–H gerilme titreşimi ve PBZ' nin alkil yan zinciri gözlemlenmiştir. Aynı numune için 1461 $cm^{-1}$ 'de gözlemlenen pikin ise benzokzazindeki benzen halkasını gösterdiği görülmüştür. 1599 $cm^{-1}$ 'de oluşan pik aromatik C = N gerinimini göstermiştir. Genel olarak tüm numunelerde karakteristik simetrik Ti – O – Ti pikleri 720–504 $cm^{-1}$ aralığında görülmüştür. Oluşan belirgin piklerle dolguların matris içinde yayılmalarından meydana gelen moleküler etkileşimler, PBZ polimerinin kendi içinde ve matris olarak nanokompozit ile etkileşimleri gözlemlenmiştir.

Hidrofobik olarak polimer nanokompozit numunelerin suyu hangi açılarla ittiğini ölçmek için numunelerin temas açısı ölçümü yapılmıştır. Bir yüzeyin hidrofobik olduğu, temas açısının 90 dereceden büyük olması ile belirlenir. Kükürt kullanılan ve kükürt ile yüksek sıcaklıkta çapraz bağlanan polimer nanokompozit film numunelerinin daha yüksek açılarla suyu ittiği gözlemlenmiştir. Kükürt eklenmemiş 25 °C'de kürlenmiş polimer nanokompozit numune suyu yaklaşık 60 derece itmiş, hidrofobik özellik göstermemiştir. Aynı sıcaklıkta sülfür eklenen polimer nanokompozit numune için temas açışı 91,8 derece iken, 180 °C'de kükürt içermeyen polimer nanokompozit numune için temas açısının 91,4 derece olduğu gözlemlenmiştir. 180 °C'de çapraz bağlanmış kükürtlü numune için temas açısı ise

101,1 derece olarak ölçülmüştür. Tüm bu temas açısı ölçümü sonuçlarına göre yüksek sıcaklıkta kükürt ile çapraz bağlanmış polimer nanokompozit numunenin en iyi hidrofobik özellik gösteren numune olduğu belirlenmiştir.

Sonuç olarak tüm test sonuçlarına göre, hidrofobik bir polimer nanokompozit hazırlanmasında başarılı olunmuştur. Katkıların homojen bir biçimde matris içinde dağıldığı gözlemlenmiş, topaklanma olmamıştır. Hazırlanan polimer nanokompozitler hidrofobik olup olmadıkları olarak kıyaslandığında sıcaklığın ve kükürt ile çapraz bağlanma yoluyla kürlenme işleminin numunelerde hidrofobikliği arttırdığı açıkça görülmüştür. Özellikle 150 °C'nin üzerinde vulkanize edilmiş kükürtlü PBZ-EPDM-PTFE-Nano TiO$_2$ polimer nanokompozit numunenin daha iyi hidrofobik yüzey özellikleri (temas açısı 110°) sergilediği belirlenmiştir.

# 1. INTRODUCTION

Polymer nanocomposites are used broadly for so many industrial applications from electronics to medical applications owing to their various functionality, light weight, low cost and suchlike properties [1]. A nanocomposite is a multiphase solid material where at a minimum one phase of dimension less than 100 nanometers (nm), or systems having nano-scale repeat distances between the different phases that composing the material [2]. They are consisting of polymer matrices, fillers and interaction zone between them.

Polybenzoxazine (PBZ) is an interesting new type of additional cure phenolic resin system matrix, especially for polymer nanocomposites. PBZs are constituted from phenol and formaldehyde in the existence of amines [3]. The diversity of content of the PBZ monomers bring molecular design flexibility which for desirable applications. Besides PBZs have some advantages like; good mechanical strength, flame retardance, dimensional stability, resistance against various solvents, near zero volumetric change, no strong acid catalyst requiring for curing, glass transition temperature (Tg) much higher than cure temperature, low water absorption [3, 4]. First benzoxazine (BZ) monomer are synthesized by Holly and Cope as different variation of 3,4-dihydro-1,3,2-benzoxazine with acid catalyst in 1944 [5]. Thence after, many researchers have synthesized varied kind of PBZs with different monomers and catalyst for deviational implementations.

One of the synthetic rubbers which is ethylene-propylene-diene rubber (EPDM) occurring the primary ingredients such as ethylene, propylene and non-conjugated dienes units in the main chain of polymer by Ter polymerizing [6-8].

EPDMs have saturated and chemically stable structure of polymer backbone which give desired properties like excellent resistance to oxidation, heat, weather aging and ozone. They are color stable that compounds of black and non-black pigmented. Due to their well responded to high plasticizer and filler loading and being inexpensive, it makes them preferable in rubber industry. It can be said that, their advantages are great

resistance to abrasion and oil swell and properties of excellent high tensile and tear in addition with flame retardance [8].

Commonly, according their ethylene content of EPDM, they are categorized as semi-crystalline or amorphous polymer. If the EPDM has 62% or more content of ethylene, they are get involved to semicrystalline polymer an if the ethylene content of EPDM is less than 62%, they called amorphous polymer. So, the crystallinity of EPDM rubber effected to content of ethylene. It can be determined via evaluating the onset temperature or the heat desired to undergo the crystalline melt. If we examine it morphologically, amorphous EPDM are more ductile and elastic and it has low hardness beside opposite to semicrystalline EPDM [9].

Owing to their brilliant thermal and chemical stability, EPDM is offering as an outstanding elastomer in various engineering applications. Regarding filler effect, the EPDM rubber systems show pretty complex rheological behavior. The significant points of these systems are short-term mechanical effect of consistent determination and long-term possessions of gum and their filled compounds. Accordingly, the estimation of those possessions becomes a challenging mission for rubber processors and final consumer. In addition of all of these advantages, the admirable electrical resistance of EPDM makes it appropriate acceptance for high voltage cable covers. The major applications of EPDM are car door seals, window and wire seals and roof system submissions [10].

## 2. EPDM RUBBER

Elastomeric systems for EPDM rubber are extremely complex formulations contingent upon their specific end-use utilization. Base elastomer, plasticizer, process oil, fillers such as mineral filler and carbon black curatives and additives are general component of elastomer formulation. It is a heterotaxic system and it was needed a certain procedure for characterized the rubber material. Thermal analysis is mostly answering the purpose of characterized the vulcanization of rubber material as time-intensive through the inevitable crosslinked system of EPDM rubber [11]. Chemical structure of EPDM rubber as shown in Figure 2.1.
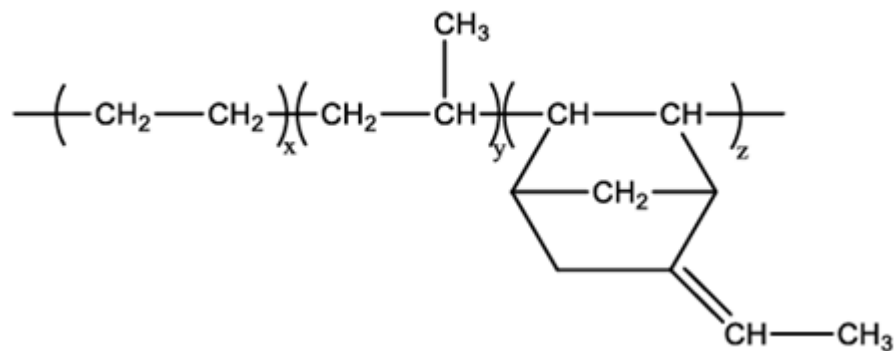


**Figure 2.1.** Chemical structure of EPDM rubber

### 2.1. Vulcanization of EPDM Rubber

Firstly, the termination of vulcanization was introduced by Brockedon [12]. Present, one of the most significant processes for rubber applications is known vulcanization, in other terms as cross-linking or curing. In the vulcanization process, the rubber material changes as high elastic product by end of the physical and chemical reactions of the rubber [13].

The major opinion of vulcanization is chemical crosslinking in rubber matrix which cause the reactions between functional groups of elastomers of three-dimensional network and suitable curing agents. There are physical couplings between elastomer

chains and many intramolecular and intermolecular tangled as hydrogen bonds, dispersion, polar forces (Figure 2.2) [14].
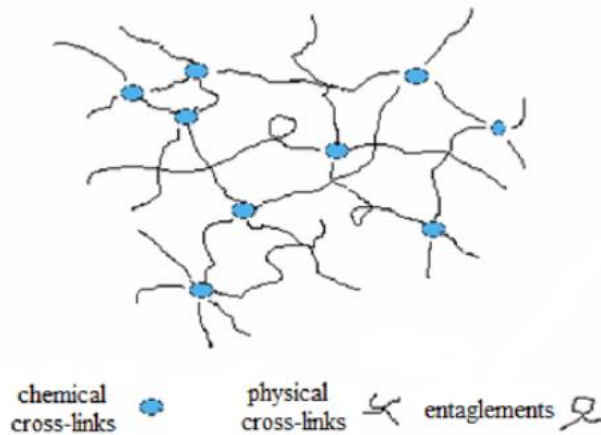


**Figure 2.2.** General schema of crosslinked network structure of vulcanizate

For vulcanization system, there are many methods, however sulfur and peroxide curing systems are most preferrable approaches. The main difference between two method is crosslinking way of elastomer chains. The sulfur systems form sulfidic cross-links different from peroxide systems of form of carbon–carbon bonds. Both vulcanization systems offer particular advantages to the cross-linked rubber articles, but also some difficulties.

## 2.1.1. Sulfur crosslinking of EPDM

For the term of crosslinking, it may be said to bring some beneficial properties like stability, strength and elasticity via including specific chemicals to elastomer. While crosslinking of rubber, the three-dimensional network points occur in the main chain of elastomer [15]. In sulfur crosslinking of EPDM rubber, sulfur interacts with double bonds of diene monomer (allylic hydrogens) of side chain of unsaturated EPDM [16].

First, the sulfur curing system reported by Charles Goodyear [17]. He heated the natural rubber with sulfur to improve physical properties of rubber. Nevertheless, he did not succeed neither good physical property nor short curing time for vulcanization process. Latest, these difficulties were solved with combination of sulfur and several accelerators to improve the rate of crosslinking and activators for the fracture of sulfur rings (S8) [18, 19].

### 2.1.1.1. Accelerator

The accelerated sulfur vulcanization is appropriate for synthetic rubbers, especially for EPDM rubber. If there is no accelerator in sulfur vulcanization, process will be longer and it won't make any sense for commercially. The requirements for accelerated sulfur vulcanization are sulfur or sulfur donors, zinc oxide, stearic acid and an accelerator or mixture of accelerators. The sulfur vulcanization system may be classified as shown in Table 2.1 depends on the level of sulfur and ratio of accelerator to sulfur [20, 21].

**Table 2.1.** The classification of sulfur vulcanization system as conventional, semi-efficient (Semi-EV) and efficient (EV)

| Type | Sulfur (S, phr) | Accelerator (A ,phr) | A/S ratio |
|------|-----------------|----------------------|-----------|
| Conventional | 2,0-3,5 | 1,2-0,4 | 0,1-0,6 |
| Semi-EV | 1,0-1,7 | 2,5-1,2 | 0,7-2,5 |
| EV | 0,4-0,8 | 5,0-2,0 | 2,5-12 |

### 2.1.1.2. Activators

The activators of sulfur vulcanization system may be called secondary accelerator [22].

The process steps for accelerated sulfur vulcanization with fatty acid and activators are presented in Figure 2.3. In step 2, the role of activators (L; amines or zinc carboxylates) is forming polysulfide ions via sulfur ring opening to enhance the vulcanization rate. To increase the efficiency of vulcanization, in the step 3 the activators role is the rubber sulfurization through enhance the concentration of accelerator. The end of the process, di- and mono sulphide crosslinks is occurring via the polysulfide crosslinks.
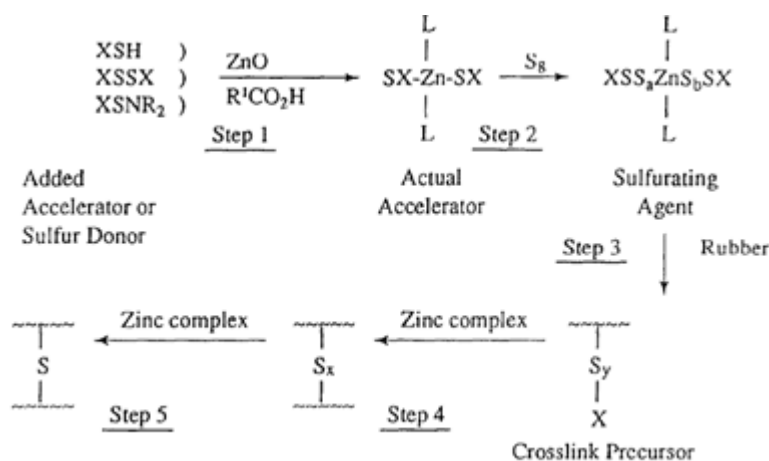
**Figure 2.3.** The role of fatty acid, ZnO and activator [22]

## 2.1.2. Peroxide crosslinking of EPDM

The main difference between sulfur and peroxide vulcanization of rubber is the peroxide crosslinking efficient in not only unsaturated rubber but also saturated rubber due to free radicals. The basic steps of peroxide crosslinking are homolytic cleavage, hydrogen abstraction and radical coupling [23].

The advantages of the peroxide crosslinking are good heat-aging resistance, simple compounding, less tension set and strain, short crosslinking time and transparent rubbers possible beside some disadvantages such as; low mechanical strength, expensive crosslinking agent and difficult hot-air cure [20, 24].

The peroxide crosslinking mechanism of homolytic cleavage, crosslinking is started by the thermal decomposition of a peroxide and formed free radicals. To form macro radicals, H-abstraction formed by the free radicals from EPDM chains. Because of the result of the large overload of aliphatic against allylic H-atoms in EPDM, H-abstraction arises probably from EPDM backbone. Consequently, the radical coupling occurs (crosslinking) in EPDM chain [25, 26].

## 2.2. Blends of EPDM Rubber

To overcome disadvantages of EPDM rubber such as poor toughening, long curing time, irreversible chemical reaction, some researchers prepared blends with various polymers. In this section, we will investigate the blends with EPDM rubber and their additional properties to EPDM rubber.

Regarding polypropylene (PP)-EPDM blends, Jain et al. examined the PP-EPDM blends effect of dynamic crosslinking on impact strength, tensile yield behavior and other mechanical properties with different wt. ratios (0-40 wt. %) [27, 28]. They observed the crosslinked PP-EPDM blend samples showed better behavior in comparison to uncross linked samples.

Siriwardena et al. [29] prepared a blend with white rice husk ash (WRHA) filled PP-EPDM for investigate effect of mixing sequence. After they tried different mixing sequences, they obtained the highest elongation at break with the sample of WRHA followed by PP were added to molten EPDM rubber.

To prepare high toughened PP-EPDM blend, Chen et al. [30] prepared a ternary blend with PP-EPDM- zinc dimethacrylate (ZDMA) via peroxide-accelerated vulcanization. ZDMA plays role as compatilizer, size reduction and improve uniform distribution of the crosslinked rubber phases. They obtained brilliant elongation and Izod impact strength in PP-EPDM-ZDMA ternary blends.

To compare fracture toughness and deformation mechanism, Haghnegahdar et al. [31] prepared nanocomposites with un-vulcanized and dynamically vulcanized PP-EPDM/graphene (multilayer graphene and few layer graphene). Regarding vulcanized samples, the main mechanism of toughness breakage derived from the formation of cavitation in the dispersed phase. And it led to the formation of nano voids within the EPDM droplets. In this fact it caused the expansion of shear bands and improvement of shear yielding of PP (matrix of blend) on the contrary in un-vulcanized samples. The graphene type contributed a various role in the fracture toughness in the PP/EPDM nanocomposites.

The presence of nano clay and silica-EPDM blends were reported [32-35]. Due to the nano clay is very strong nanofiller, the EPDM-polymer blends have outstanding mechanical properties according to these studies.

The EPDM blends with carbon allotropes such as graphene ball [36] and carbon nanotube [37] were reported for improve the thermal conductivity and ablation resistance. Some researchers reported EPDM blends with other kind of rubbers such as natural rubber [38-42], styrene butadiene rubber (SBR) [43], silicon rubber [44], nitrile butadiene rubber (NBR) [45-47] to improve properties of EPDM rubber.

## 3. POLYBENZOXAZINE (PBZ) POLYMERS

### 3.1. Classification of Benzoxazine Monomer

BZs are classified according to their functionality of the BZ monomers, dimers and oligomers. The reason of the classification is that PBZ are used for varied executions regarding their functionality of the additional substituting groups. These groups also qualify the curing process of the BZ and determine the application area of the PBZ resin.

### 3.1.1. Monofunctional

As stated previously, Holy and Cope synthesized first well defined BZ monomer as condensation reaction of phenol and formaldehyde in the existence of primary amines [5]. In the Figure 3.1, X and R' are substituent, like $CH_3$, $C_2H_5$, and benzene.
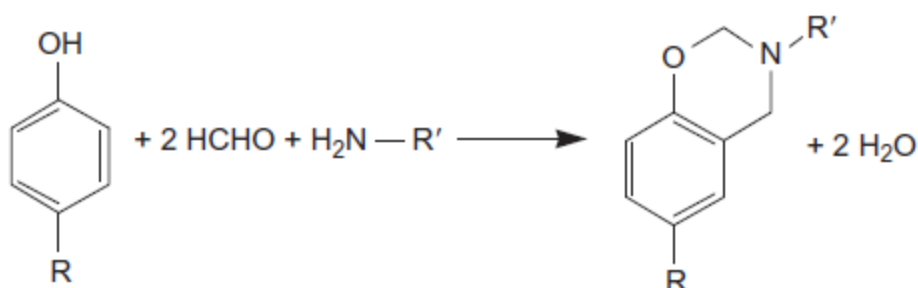


**Figure 3.1.** Synthesis of benzoxazine resin

They synthesized monofunctional BZ monomer as procedure with acid catalyst within the solvent. Following, Mannich bridge was observed by Burke [48] as BZ rings react to phenolic compounds' free ortho positions. He synthesized 3,4-dihydro-3,6-disubstituted-1,3,2H-benzoxazines as reaction of p-substituted phenols with formaldehyde and primary aliphatic amines in a molar ratio 1:2:1, respectively. To exemplify, for synthesize 3,4-dihydro-3-cyclohexyl-6-t-butyl-1,3,2H-benzoxazine there were two procedures which he applied in same study.

In the first procedure, Cyclohexylamine was joined together with cooling to dioxane containing aqueous formaldehyde through dribs and drabs. Following supplementation of p-t-butylphenol the mixture was heated and refluxed within 2 hours, then the crystalline product was obtained after cooling room temperature. Finally, the crystalline product was recrystallized from 95 % ethanol and 78 % of efficiency.

In the second procedure, paraformaldehyde was deliquated in warm methanol within potassium hydroxide. Then it was followed the cooling step with addition of cyclohexylamine as similar with first procedure by dribs and drabs and was added p-t-butylphenol for obtained solution of product. The solution was heated under reflux for fifteen minutes, and then after cooling step, the crystalline solid was recrystallized from 95% ethanol, and 92% of efficiency.

Kimura et al. [49] synthesized bisphenol-A based BZ without a curing accelerator. They followed similar procedure with Ning and Ishida [50]. In this procedure they used ice bath different from other previous studies. They prepared a mixture with formaldehyde, dioxane and methylamine to keeping temperature below 10 ℃. Then it was added bisphenol A and raised the temperature then after the mixture solution was allowed to reflux for 6 h. After decontamination step, it was obtained final product.

All these kinds of procedures which has been reported were led to some disadvantages about by-product in the BZ. Because of the ring opening polymerization (ROP) and stability of benzene ring, Mannich bridge caused small oligomer. Also, some researchers were getting other problems about pure solubility of the precursors, slow reaction rate and especially requiring big amount of solvent and it was giving expensive procedure. For sure, it was caused to make it difficult to remove solvent.

To overcome these disadvantages, Ishida [51] synthesized and get patent solventless procedure of BZ. He observed the fast reaction rate, single step procedure and eliminate toxic solvents, when he compared with previous studies. After that it was studied different catalysts for reduce the curing temperature and time [52], another method for synthesis PBZ with monofunctional BZ was reported by Li et al. [53] and Chen [54], BZ without catalyst for resin transfer molding reported by Xiang et al. [55].

Reiss et al. [56] in 1985, worked with the reaction kinetics of BZ oligomer formation using mostly the monofunctional BZ, showing that large molecular weight linear PBZ

cannot be obtained from monofunctional BZ. Only, if the benzene ring is adequately reactive, even a monofunctional BZ resin can induce a crosslinked polymer.

Recently, Ohashi et al. [57] studied with monofunctional BZ substituted by electron donating or withdrawing group. They studied the quantitative effect of the substituent for approximately predict to the polymerization temperature of different kinds of BZ by focusing on their substituents before their synthesis.

### 3.1.2. Difunctional

Difunctional BZ resins comprises the use of a difunctional phenolic compound and a diamine bringing a linear polymer having oxazine rings in the main chain. Only, according to reactivity of the benzene rings it can be seen small branch areas. In the Figure 3.2 as shown below, there is main-chain type PBZ that is based on bisphenol and diamine. In the main chain, the polymer may be more cross-link through the oxazine ring polymerization.
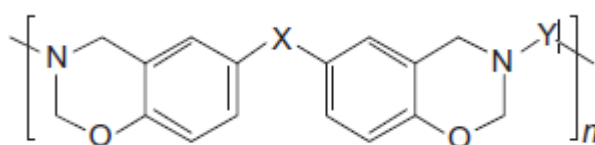


**Figure 3.2**. General chemical structure of PBZ

Monomeric type difunctional BZ resins based on bisphenol and monoamine, or diamine and phenol as shown in Figure 3.3a and Figure 3.3b. R is a group, like $CH_3$ and other aliphatic groups, or substituted benzene rings, and X is a group, like $CH_2$, $C(CH_3)_2$, $C(CF_3)_2$, $C_{1/4}O$, $SO_2$. It can be used any combination of a bifunctional phenol and primary amine in the Figure 3.3a. Also, there are different combination of a bifunctional amine and mono-functional phenol like Figure 3.3b, however it can be affected the structure of crosslinked polymer.
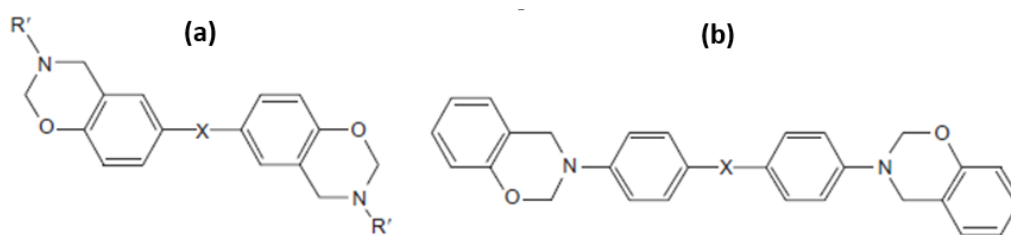


**Figure 3.3.** Different combinations of a bifunctional phenol and primary amine

Kimura et al. [58] studied to reduce the curing time and lower temperature of the BZ compound with difunctional BZ monomers using aniline instead of methylamine. They investigated difunctional BZ with latent curing agent showed superior heat resistance, mechanical properties, flame resistance and electrical insulation properties because of higher crosslinked density.

Brunovska et al. [59] investigated bis(3,4-dihydro-2H-3-alkyl(aryl)- 1,3-benzoxazinyl) isopropane in the existence of both solvent and primary amine. For the solventless synthesis of BZ, 1,3,5-triphenylhexahydro-1,3,5-triazine was used for source of amine instead of direct use of primary amine.

Low et al. [60] synthesized difunctional BZ with aniline, paraformaldehyde, and some kind of phenols such as p-cresol, bisphenol-A, hydroquinone, 2,20-biphenol, 4,40-dihydroxybenzophenone, 4,40-thiobiphenol, 1,5-napththol, and 1,1,1-tris(p-hydroxyphenyl) ethane, in solventless system. They investigated the Mannich base was steady going for all kind of phenols, however the char yield of the BZ was showed different behavior because of their incompatible linkages. Also, the initial rate of the weight loss was influenced. According to oxidative degradation of the benzoxazine, the effect of the different phenols is found to be notable below 600 °C.

### 3.1.3. Multifunctional

Multifunctional BZ consist of multifunctional amines or phenolic derivatives can also be used to synthesize for large molecular weight linear PBZ. First it was reported the use of multifunctional phenol and amine for small molecular weight BZ in their patent [61]. So many studies were reported for small molecular weight BZ after that. Then, Subrayan et al [62] synthesized melamine-based resin system for potentially low-cost route of crosslinked multifunctional BZ.

Mohamed et al. [63] synthesized new multifunctional BZ monomer which is Azo-COOH-Py-BZ with azobenzene unit, 4-(4- hydroxyphenylazo) benzoic acid (Azo-COOH), paraformaldehyde and aminopyrene (Py-NH$_2$). They investigated lower thermal curing temperature than the traditional pyrene-based BZ monomer, because the azobenzene and COOH units behaved as catalysts for the thermal curing process.

Y. Murai et al. [64] synthesized high molecular weight BZ with different monomers such as bisphenols and diamines. They prepared films with different combination of bisphenols and diamines to improvement mechanical and thermal properties of PBZ.

### 3.1.4. Combination with polymerizable group by itself

### 3.1.4.1. Acetylene containing monomer

This kind of monomer is one of the free radically polymerizable group. The oligomers and polymers containing an acetylene group lead to be polymerized without the evolution of volatiles. The acetylene containing BZ monomer ensures several properties, like solvent resistance, moisture resistance, good physical properties and high thermal stability. The acetylene group be able to give reaction under cationic, coordination, free radical, photolytic and thermal stimulation. The thermally induced reaction of the acetylene group involves chain extension, branching, or cross-linking of the polymer [65].

Kim et al. [66] investigated acetylene containing BZ monomer of dynamic moduli and glass transition temperature of the polymerized resin. The acetylene containing BZ monomers were synthesized with the novel solventless technique and others were synthesized with solvent. When comparing both acetylene containing BZ monomers, they showed higher Tg from process temperature and there was no need to catalyst as well.

Liu et al. [67] prepared a copolymer with acetylene containing BZ and bisphenol A diglycidyl ether (DGEBA) epoxy resin without curing catalyst. They investigated to improve their processibility and adhesive properties without reducing much thermal performance. The cure blends were showed good heat and water resistance properties and high Tg.

Sun et al. [68] synthesized ortho amide functional BZ containing acetylene and they investigated dielectric properties of the thermosets. When they characterized the samples, they obtained high thermal stability, high char yield value and very low dielectric constant and it can be good applicant for the high-performance area.

Yang et al. [69] prepared a blend with bismaleimide acetylene containing BZ. They synthesized 6,6′ -(propane-2,2-diyl) bis(8-allyl-3-phenyl-3,4-dihydro-2H-benzo[e] [1,3] oxazine) (DBA-a) and 6,6′-(propane-2,2-diyl) bis(8-allyl-3-(3-ethynylphenyl)-

3,4-dihydro-2H-benzo[e] [1,3] oxazine) (DBA-ac) with 2,2′ -diallyl bisphenol A (DBA), aniline and paraformaldehyde to reduce the polymerization temperature and improve the exhaustive properties. To applied different strategies such as chemical modification with acetylene and blending with bismaleimide. It was reported very high-performance thermosets based on BZ chemistry and resin blending.

### 3.1.4.2. Allyl-containing monomer

The other free radical polymerizable group is allyl-containing BZ monomer. This kind of monomers are used as reactive diluents of bismaleimides to improve the toughness of the cured resin [70]. They are ensured additional cross linkable sites [71] and might be polymerized themselves, easily cured because of lower cure temperature [72].

Ishida et al. [73] prepared a composite with glass-fiber-reinforced PBZ. The allyl containing monomer was synthesized from tert-Butyl amine because of helping oxazine ring formation as shown in Figure 3.4. Also, they studied with phenol to synthesize allyl containing BZ monomer.
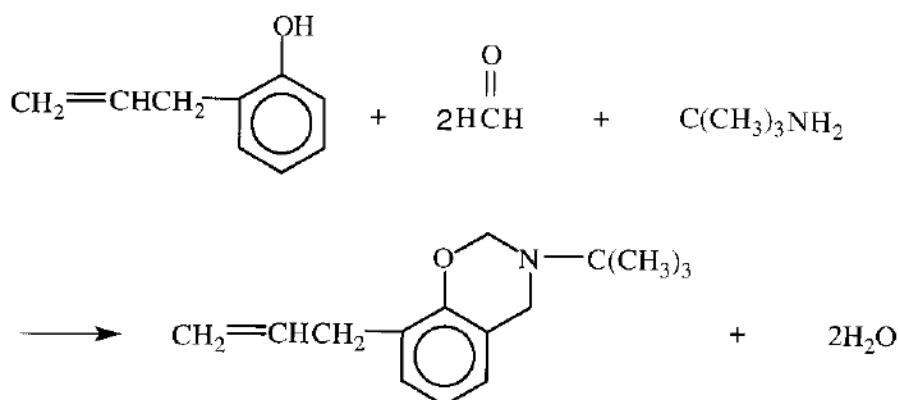


**Figure 3.4.** Synthesizing step of allyl containing BZ monomer [73]

Agag and college synthesized 3-allyl-3,4-dihydro-2H-1,3-benzoxazine and bis(3-allyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane from phenol and Bisphenol-A with allyl amine and formaldehyde. They were used two ways to synthesize allyl containing BZ monomer and they observed both of them showed better thermal stability from BZ monomer without allyl functional group [74].

K.S. Santhosh Kumar et al. concentrated to improve PBZ properties of crosslinking and ROP with allyl terminated BZ monomer [75]. It was synthesized 2,20 -bis (8-allyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane from bis benzoxazine monomer

having allyl groups at the ortho positions of phenol as shown in Figure 3.5. Consequently, they observed high crosslinked density, good thermal stability and high Tg.
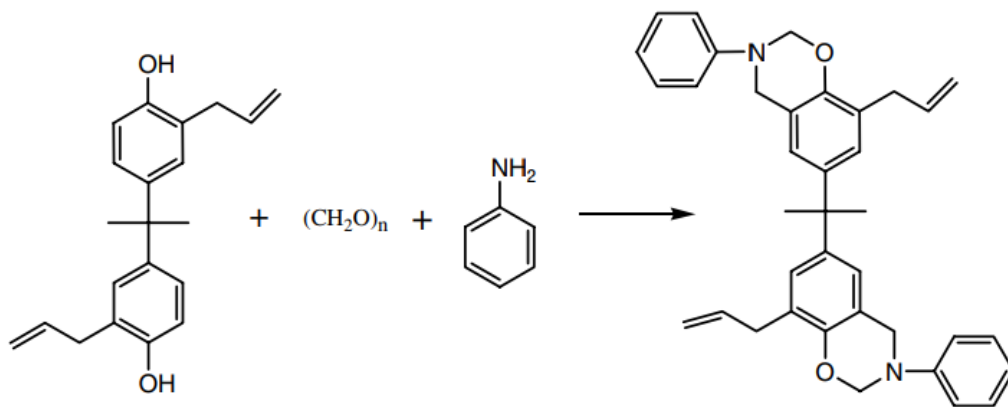


**Figure 3.5.** Synthesizing of allyl containing benzoxazine monomer [75]

Takeichi et al. synthesized aniline and allylamine-based benzoxazine monomers from cresol, aniline and allylamine, paraformaldehyde using the solventless method [76]. They marked allylamine-based monomers were highly achievable to polymerize at below 150 °C, but for ring opening process they needed 250 °C to obtain PBZ.

Wang et al. prepared a blend with 2,2' -bis(8-allyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane (Bz-allyl) and N,N' - (2,2,4-trimethylhexane-1,6-diyl) di maleimide (TBMI) [77]. When we compared with previous investigations, it was observed some different results about curing mechanism. It was reported just 20% of TBMI reacted with allyl groups, some TBMI reacted through thermal reaction and others catalyzed by allyl containing BZ. They reported Tg was shifted to higher temperature by increasing the TBMI content of the blend.

### 3.1.4.3. Epoxy containing monomer

The epoxy-containing BZ monomers used to improve mechanical and thermal properties of benzoxazines by some researchers, but mostly epoxy was used as copolymer with BZ. One of researcher who studied with epoxy as functionalized to BZ, synthesized from aniline and 4-hydroxybenzoic acid and from phenol and 4-aminobenzoic acid [78]. They studied the process with and without catalyst and they obtained different results as shown in synthesizing scheme (Figure 3.6). In the scheme, M-1 is epichlorohydrin and M-2 is glycidylic derivatives. For M-2, when boron

trifluoride monoethylamine (BF3-MEA) was used as a catalyst, the epoxy and BZ ring openings could be individuated, it could be acquired a polyether intermediate.
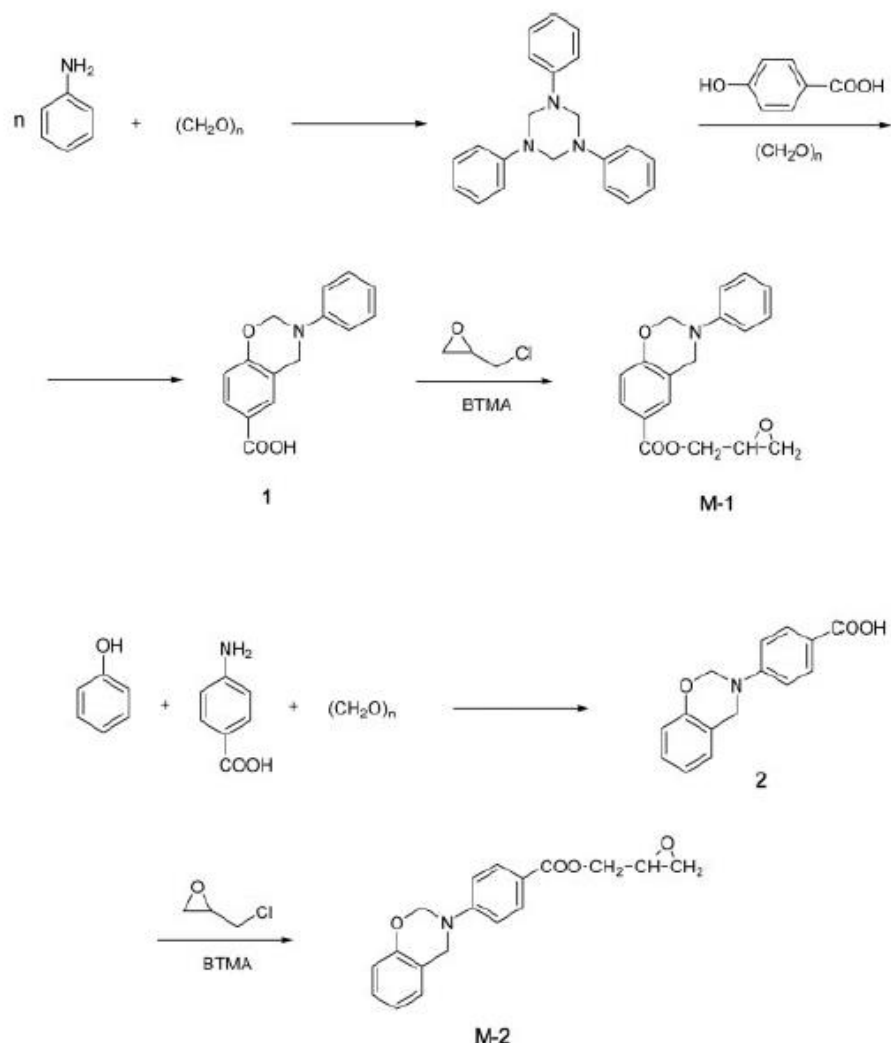


**Figure 3.6.** Synthesizing schema for epoxy containing BZ monomer [78]

### 3.1.4.4. Nitrile and phthalonitrile-containing monomers

The phthalonitrile-containing BZ monomers bring thermal stability and processability to PBZ resins because of the curing temperature and viscosity higher then without nitrile-containing PBZ resins [79]. Also, these kinds of monomers give side functionality to help cross-link network formation by its own polymerization [80].

Cao et al. [81] synthesized the bisphthalonitrile-containing BZ from bisphenol-A, 4-aminophenoxylphthalonitrile and paraformaldehyde. They observed the polymerization was occurs as two step which is o oxazine ring-opening and phthalonitrile ring-forming. The results of their study were showed the polymer of char yields above 73% in nitrogen at 800 °C and above 78% in air at 600 °C. Also, the

cured resin was showed good thermal stability and thermos-oxidative stability according to their characterization results.

Zuo and Liu [82] synthesized this BZ monomer from 4,4'-dihydroxybiphenyl, paraformaldehyde, and 4-aminophenoxylphthalonitrile with solventless method and two step polymerization as previous study. They used 4,4' -diaminodiphenylsulfone and FeCl$_3$ as catalyst and these catalysts were helped to increase the curing rate and low cure temperature. According to results of characterization, they obtained the char yield was 76.0% by weight at 800 °C under nitrogen atmosphere and 81.2% by weight at 600 °C under the air.

Yang et al. [83] designed a low-temperature curable phenolic/benzoxazine-functionalized phthalonitrile copolymers for high performance glass fiber (GF) composite laminates from bisphenol A-based benzoxazine-functionalized phthalonitrile. They succeeded to prepared the composite with low process temperature for composite (160 °C), low cure temperature, short process time and low process pressure.

Zhang et al. [84] investigated about flammability of the thermosets with synthesizing phthalimide and nitrile-terminated benzoxazine (2-(8-(1,3-dioxoisoindolin-2-yl)-2H-benzo[e] [1,3] oxazin-3(4H) yl) benzonitrile (oPP-an) from xylenes, anthranilonitrile, o-PP, and paraformaldehyde. They obtained short reaction time for BZ monomer (8 hr), high yield which was 91%, high thermal stability with a high temperature (550 °C) and high char yield value (70%) and magnificently low flammability with a low heat release capacity (HRC of 30.1 J g$^{-1}$ K$^{-1}$) and low total heat release (THR of 7.6 kJ g$^{-1}$).

### 3.1.4.5. Maleimide-containing monomer

The maleimide provides low melting point, low polymerization temperature, high reactivity of polymerization, high Tg and so forth to BZ monomer [85].

To improve thermal properties, Ishida and Ohba [86] synthesized two forms of monofunctional benzoxazines through maleimide functionalities. Because of functionalities of maleimide and norbornene, they achieved to synthesize benzoxazines with more polymerize from general BZ monomers. Their other purpose was achieved high performance polymers from low viscosity BZ monomers in high Tg. They obtained high char yields (above 55%), and high Tg (above 250 °C) for their

PBZ. Also, they studied Maleimide based BZ monomers copolymer with epoxy to recover hardiness and processibility without bargaining the thermal properties [87]. If we compare their studies in this content, maleimide-epoxy copolymer was showed higher Tg from previous work about maleimide containing BZ. They observed different content of epoxy (diglycidyl ether of bisphenol-A) in the maleimide-epoxy copolymer showed different flexural properties.

Due to not clear the effect of curing behavior into before studies, Liu and Yu [88] investigated cocuring behaviors of maleimide containing BZ monomers. They observed different maleimide compounds affected to curing behavior and crosslinking networks of BZ monomer, in different way. For instance, if maleimide compounds having acidic groups, it exhibited an acid-catalytic effect on the polymerization of PBZ. Acid catalyst reaction set up chemical linkages between the crosslinked networks of BZ and maleimide and is predicated to the high Tg and good thermal stability of the polymers.

Y. Tang et al. [89] showed effect of allyloxy groups of maleimide containing BZ monomer. They observed the allyloxy groups decreased the melting point and showed symmetric exothermic peak in DSC curve.

L. Jin et al. [90] studied a different class of bis(benzoxazine-maleimide) monomers as high-performance thermosets from hydroxyphenylmaleimide. The thermally activated polymerization resides ROP from BZ and addition polymerization from maleimide. The crosslinked polymers showed great thermal stability and high Tg along with easy processibility, representing synergistic effect of BZ and maleimide resin.

### 3.1.4.6. Propargyl-containing monomer

Propargyl-ether terminated BZ monomers come from acetylene terminated monomers. They give free radical end capping agent to the network of monomer. Owing to this property, they can be easily synthesized and requirement low cost unlike ethylene terminated BZ monomers and they can be improved thermal properties of PBZ [91].

To synthesize thermally stable PBZ, Agag and Takeichi [92] provided BZ monomers containing arylpropargyl ether. They used monofunctional and bifunctional BZ monomers together and succeeded high char yield (approximately increased 22-29%) and high Tg (approximately increased 100-140 °C) in contrast to general BZ monomers.

B. Kiskan and Y. Yagci [93] synthesized propargyl ether containing BZ monomer and prepared PBZ using rhodium catalyst. They obtained thermally activated self-curable PBZ due to absence of BZ functionality. Which shows that polyacetylene containing BZ side groups endures irreversible cis–trans isomerization and thermally activated curing without any catalyst making polyacetylene thermoset with high thermal stability.

### 3.1.4.7. Glycidyle-containing monomer

These kind of BZ monomers interest with mostly thermal and flame-retardant properties of PBZ. Such as Espinosa et al. [94, 95] investigated curing and crosslinking behavior and thermal properties of glycidyle containing BZ monomers. They recommended to modify novalac resins with glycidyle-containing BZ monomers as crosslinking agent and they reached industry standard for flame retardancy.

Another work for glycidyle-containing BZ monomer was studied by M. Sponto´n et al. [96]. They used three step synthesis unlike general synthesis BZ. Firstly, 2-hydroxybenzaldehyde was reacted with bis(m-aminophenyl)methylphosphine oxide. The consequential imine compound was condensed in situ with $NaBH_4$ at room temperature yielding the o-hydroxybenzylamine derivative. Consequently, after adding paraformaldehyde in dioxane the BZ derivative was acquired with 95% of yield. The characterization values of limiting oxygen index were meaningly higher for the BZ–epoxy systems.

### 3.1.4.8. Methacrylate-containing monomer

For this section, Tasdelen et al. [97] studied photoinitiated free radical polymerization using methyl methacrylate BZ as hydrogen donors. They achieved at wavelengths of $\lambda > 350$ nm with the aid of aromatic carbonyl photosensitizers with methyl methacrylate BZ.

Koz et al. [98] synthesized BZ monomer with methacrylate functionality which name of 2-(2-(2H-benzo[e][1,3]oxazin-3(4H)-yl)ethoxy) ethyl methacrylate. They investigated thermal properties, cure structures and crosslinking behavior of BZ monomer and achieved to obtain easy polymerize and thermally stable copolymer.

### 3.1.4.9. Oxazoline containing monomer

The oxazoline containing BZ monomer is a good candidate, due to oxazolines show good flowability below 140 °C, curing reaction progressed above 180 °C rapidly, and it has superior heat resistance, electrical insulation, and water resistance. It helps to improve the crosslinking density, low curing time and low curing temperature for BZ monomers [99].

Chen et al. [100] prepared a nanocomposite with octaaminophenyl polyhedral oligomeric silsesquioxane and modified BZ with 2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles) by solvent methods. According to characterizing methods, they obtained higher Tg and thermal stability than pristine PBZ.

Cao, Xu and Yu [101] synthesized 2-oxazoline-benzoxazine with 2-(hydroxylphenyl)-2-oxazoline, 1,3,5-triphenylhexahydro-1,3,5-triazine and paraformaldehyde. They prepared a compound and its PBZ. DMA and TGA results exhibit that the thermal properties of oxazoline based PBZ are better than the common polymer of BZ and the composite material of 2-oxazoline and benzoxazine. Due to the BZ monomer generates less deficiency during polymerization than BZ precursor with oligomer.

To reduce the curing time, to the lower the cure temperature and higher crosslinking density of BZ compound, Kimura et al. [102] prepared cured BZ resin with bisoxazoline or epoxy resin using the latent curing agent. Eventually, because of phenol-novolac based BZ had a lot of oligomers and phenolic hydroxyl group, they obtained low cure temperature with the latent curing agent.

### 3.1.4.10. Norbornene containing monomer

Some researchers investigated norbornene BZ monomer with imide functionality. To develop low viscosity BZ monomer and obtain high performance PBZ, Ishida and Ohba [103] studied synthesis and characterization of norbornene functional BZ monomer. They observed curing effects using three different free radical initiators like 2,2'-azobisisobutyronitrile, benzoyl peroxide and dicumyl peroxide at three different temperatures and thermally activated polymerization of BZ monomer. Consequently, they achieved high char yield and high Tg without increasing viscosity of BZ monomer importantly.

Because of previous study required high boiling point solvent and high reaction time, Zhang and their coworkers [104] synthesized monofunctional and difuntional BZ with norbornene. They purposed adding more study to ortho functional BZ and showing different polymerization method except general methods of synthesizing PBZ. They obtained short reaction time, high char yield (61 %), high thermal stability with Tg of 365 °C and effortlessness of purification from solvent to BZ monomer.

According to these studies, BZ monomers with norboranane presented improved thermal properties, network structure and ensuring extra crosslinking.

### 3.1.4.11. Vinyl ester containing monomer

To better understand interaction of hydrogen bonding between PBZ and PBZ with vinyl terminated BZ monomer, Su et al. [105] prepared a blend system. It is important to understand crosslinking behavior of obtained PBZ. According to characterization results, they obtained good interrelation between DSC and FTIR analysis.

Lee et al. [106] prepared a nanocomposite with vinyl-terminated BZ monomer and polyhedral oligomeric silsesquioxane (POSS) to improve thermal stability of BZ monomer. They observed the presence of vinyl terminated PBZ with POSS, relatively high thermal stability than general PBZ with POSS. Tg value was increased from 307 °C to 333 °C for the nanocomposite with vinyl terminated PBZ and weigh 5 wt% of POSS.

Another vinyl terminated BZ blend with poly (ethylene oxide) were prepared by Huang et al. [107]. After applying different weigh ratios of component of blend, they achieved high Tg, increased hydrogen bonding, high crosslinking with 50/50 poly (vinyl BZ)/poly ethylene oxide) blend.

Huang and Kuo [108] prepared a PBZ nanocomposite with multifunctional POSS cores presenting vinyl-terminated BZ monomer at different compositional ratios. They obtained thermal and mechanical stability due to OH groups from PBZ and hydrogen bonding between the siloxane group of POSS cores.

Vinyl ester gives rapid reaction due to their polymerizable groups with photopolymerization also they have rich molecular design flexibility and inexpensive applying to BZ monomer.

### 3.1.5. Combination with potentially polymerizable group with appropriate partners

Commonly, these partners associate with condensation polymerization mechanism which are phenol, primary amine, methylol, ethylol, hydroxy ethylether, aldehyde, azide, carboxylic acid and isocyanate.

Carboxylic acid partner acts as catalyst for BZ monomer in literature, regularly. First, Dunkers and Ishida [109] discovered the effects of curing 3,4- dihydro-3,6-dimethyl-2H-1,3-benzoxazines to PBZ. They used and compared strong and weak carboxylic acid and phenol as catalyst. They observed using weak carboxylic acid as catalyst showed auto-accelerated reaction instead of strong acid. Using strong acid, there is no delay between the ring opening and Mannich bridge formation reactions caused by the attendance of a reactive entrepreneur in their study.

Kim and Ishida [110] synthesized PBZ in carboxylic acid solution. They achieved stable Mannich base in parallel with chemical stability of PBZ and strength of the hydrogen bonding network.

Andreu et al. [111] described various carboxylic acid containing BZ monomers by autocatalytic thermal polymerization. They considered thermal stability and flame retardancy of PBZ with carboxylic acid catalyst and they gained them along with high Tg.

BZ containing maleimide and carboxylic acid was synthesized by Zhong et al. [112]. They prepared 1-[3-(4-carboxylphenyl)-3,4-dihydro-2H-benzo[e][1,3]-oxazin-6-yl] maleimide and characterized HNMR and FTIR. According to DSC and TGA analysis, they reached high Tg and high char yield for carboxylic acid containing BZ monomer.

Primary amine is one of the main components of general PBZ. There are various studies about primary amine to synthesize BZ monomer as we investigated in previous titles. Agag et al. [113] synthesized primary amine functional BZ monomer included with amide containing BZ monomer. They achieved to improve reactivity of BZ monomer.

Methylol and ethylol generally play a role on BZ's crosslinking formation. Baqar et al. [114] studied kinetics of polymerization of PBZ and investigated the impression of integrating methylol groups into BZ monomers. Furthermore, they succeeded to

decrease the polymerization temperature. Zhang et al. [115] obtained remarkable thermal stability with adding para-methylol to BZ monomer.

In the near future, Lee et al. [116] used isocynate to functionalized BZ monomer and they prepared a powder coating with bismaleimide for high temperature and high-pressure applications. They obtained high Tg, extraordinary wet adhesion, water repellency and toughness for end product.

### 3.1.6. Reactive polybenzoxazines

### 3.1.6.1. Main-chain type

High molecular weight PBZ can be synthesizing with different sort of precursors. It is significant for various properties and quality of PBZ. Despite, because of the morphology of polymers, PBZs have various chain ends due to synthesized from kinds of BZ monomers. The serious problems are crosslinking density and low molecular weight be directly affected to mechanical and thermal properties of PBZ. Thence, the solution will be reducing the concentration of the unpolymerized chain ends. Containing oxazine rings in the main chain of PBZ [117], effect of temperature [118], solvent [119], reactant ratio and catalyst worked by some researchers. Conditions of Mannich reaction of PBZ is the main point of this problem. The density of the ring-closed structure in Mannich bridge of PBZ should be high enough for polymerization. Takeichi et al. [120] synthesized PBZ with aromatic or aliphatic diamine and bisphenol-A and paraformaldehyde. They obtained high crosslinking density and high aromatic content in parallel with high thermal stability. Chernykh et al. [121] synthesized PBZ with a phenol, formaldehyde, and an amine for Mannich reaction. According to quantitative end group analysis, they received very high yield PBZ.

Currently, Ohara et al. [122] prepared high molecular weight BZ monomer with dialdehydes from diamines, formaldehyde, and hydroxybenzaldehyde by a two steps method. They synthesized PBZ having azomethine linkages because of their exceptional thermal properties. They aimed to improve thermal and mechanical properties in parallel with high Tg, toughness and high heat resistance.

### 3.1.6.2. Side-chain type

To overcome low density of crosslinking of PBZ, researchers have been investigated side chain type BZ monomers. The based on polyphenylene of side chain precursors

are reported by Kiskan et al. [123]. They synthesized 3-phenyl-3,4-dihydro2H-benzo[e][1,3] oxazine by oxidative polymerization. After curing step, high thermal stability and low conductivity have been exhibited by oxidative PBZ.

Ganfoud et al. [124] used cardanol as alkyl side chain on BZ monomer. Actually, cardanol long alkyl side chain brings a plasticizing effect to BZ monomer and cost a lower degree of polymerization. Accordingly, Tg was decreased but, somehow the thermal stability is suggestively improved for cardanol-based PBZ, due to H-bonds on the aliphatic chains.

Sharma et al. [125] functionalized side chain type BZ monomer with polyethylenimine. They aimed to synthesize nitrogen-enriched side chain type BZ monomer using various bio-based phenols and polyethylenimine. Before, they reported an article using guiacol and polyethyleninine and they optimized the reaction limits like reaction medium, time, and stoichiometry. They observed the better molar ratio of guiacol polyethylenimine resins prepared at 8:1:16 and 10:1:20 respectively phenol, amin and paraformaldehyde.

### 3.1.6.3. Telechelic

Telechelics means to contain functional groups in macromonomers. They can be used for block and graft copolymers as cross-linkers, chain extenders, and precursors. Yıldırım et al. [126] used Poly(propyleneoxide) amines for naphthoxazine units as crosslinking agent. They observed the molecular weight of the initial polymer increased, the reduction of amino groups to naphthoxazine was decreased. The hydrophilic PBZ was obtained according to surface analysis characterization. Nakamura and Ishida [127] synthesized telechelic BZ monomer consuming oligomeric bisphenols through aromatic ether structure. In this work telechelic property used as crosslinking agent and showed thermoplastic-like behavior for PBZ.

### 3.2. Reaction Mechanism of Ring Opening Polymerization of Polybenzoxazine

To understand oxazine ring and Mannich reaction is so significant for understanding ROP of PBZ. For the oxazine ring structure, there is a nitrogen and oxygen in benzene ring and there is a tension in carbon between oxygen and nitrogen due to their molecular conformation. This tension helps to their ring opening reaction under special circumstances. Accordingly, because of the oxygen and nitrogen have high basicity,

they may act as possible cationic polymerization induction sites and makes the ring very potential to open through a cationic mechanism [128]. Firstly, the ROP was reported by Burke et al. [129]. They investigated the Mannich bridge in the reaction of 1,3-dihydrobenzoxazine with a phenol. They have both ortho and para positions free and occurred aminoalkylation that form a Mannich bridge. To clarify this ortho preference the formation of an intermolecular hydrogen-bonded middle types was proposed. Another study was showed the high reactivity of ortho position in monofunctional BZ catalyst with 2,4-di-tert-butylphenol [130].

The classification of ROP as following chapters.

### 3.2.1. Thermal polymerization of polybenzoxazines

In industrial applications, the most applicable method for synthesizing PBZ is thermal polymerization ROP. Some researchers showed that the only requirement was heat for synthesizing PBZ. There was no need to add any participating for polymerization. Thence, under such circumstances, benzoxazines are polymerized overall a solid thermal polymerization. There is a difference between thermally activated or accelerated polymerization in the literature. In thermally activated polymerization, there are some impurities and additives such as catalyst and or initiators. In the Figure 3.7, the difference between them can be seen obviously [131].
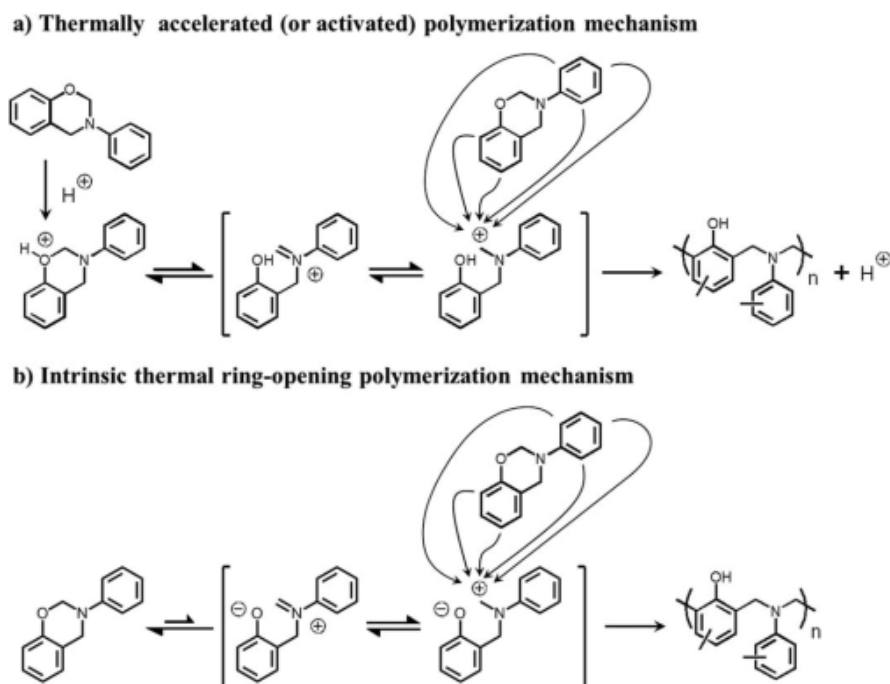


**Figure 3.7.** The difference mechanism between thermally accelerated ROP and thermal ROP [131]

The PBZ that has high crosslinking density may be synthesized with monofunctional and difuntional BZ monomer by thermal polymerization ROP [132].

Noticeably, in the thermal ROP, the diamine based difunctional BZ monomers are anticipated to resemble crosslinking structure. They compared the DSC diagrams for monofunctional and difunctional BZ monomers. They observed the difunctional BZ monomer showed higher exotherms than monofunctional BZ monomer because of during synthesis difunctional BZ monomer formed small oligomers and dimers along with major product. It means, there was higher crosslinking structure within difunctional BZ monomer.

To understand thermal ROP as kinetics and cure mechanism, BZ monomers can be characterized with DSC, FTIR, DMA, 13C and 15N solid state NMR.

### 3.2.2. Cationic polymerization of polybenzoxazines

To overcome some disadvantages of PBZ like long reaction time, some researchers used catalyst and initiators in or during polymerization. If the catalyst or initiator that used is cationic, the ROP called cationic ROP [133].

In this section, the iminium ion structure occurs with oxazine ROP thanks to oxygen protonation. The reactive electrophilic aromatic substitution would form via interaction between the ortho position of the phenolic benzene ring and methylene group. In addition of the phenolic polymers, also the phenoxy polymers produced. Generally, phenoxy polymers reorder as phenolic polymers to used ROP afterwards [134].

### 3.2.2.1. Base catalyzed polymerization of polybenzoxazines

In cationic polymerization of PBZ, if it used base catalyst for polymerization of PBZ, it called base catalyzed cationic ROP. To choose catalyst is significant for ROP due to their recovering properties for polymerization and properties of final product PBZ. The adding catalyst to BZ monomer effect was studied by Baqar et al. [135]. They used 1-methyl-imidazole and compared p-toluenesulfonic acid (PTSA) and lithium iodide (LiI).

Endo and Sudo [136] used 2-(N,N-dimethylamino)ethanol (DMAE) as base catalyst for polymerization of N-methylbenzoxazine. They compared the reactivity of N-(2-hydroxyethyl) benzoxazine and N-methylbenzoxazine polymerization in existence of

DMAE. Because of the amount of hydroxyl groups formed covalent bonding with BZ monomer, DMAE can be accelerated the mechanism of polymerization of both BZ monomer with different polymerization ratio.

### 3.2.2.2. Acid catalyzed polymerization of polybenzoxazines

As we known, there are some disadvantages such as long reaction time and non-polymerizable groups in the main chain of polymerization of PBZ. To defeat them, some researchers getting help from organic acids and Lewis acids to catalyze the polymerization PBZ.

Dunkers and Ishida [86] used strong and weak carboxylic acid as catalyst to synthesize 3,4- dihydro-3,6-dimethyl-2H-1,3-benzoxazines to PBZ. They observed effect of catalysts to curing kinetics, reaction rate and existence of side reactions of PBZ. Regarding the test result, they reported the weak carboxylic acid acted like autocatalytic effect to PBZ unlike the strong carboxylic acid. The strong carboxylic acid caused poor formation of Mannich bridge reaction because of reaction time is too fast and short.

For cationic mechanism of ROP of PBZ, the anionic, cationic and radical initiators that used were reported [137, 138, 141, 142]. According to studies, when there was no catalyst but the curing temperature around 160 °C – 170 °C, phenol may be catalyzed to ROP system [86, 139]. Zhang et al. investigated self-catalyzed cationic ROP due to their phenolic OH formed to polymerization of oxazine. They observed phenol may act autocatalytic effect to ROP system.

Regarding some investigations, $PCl_5$ can be catalyzed to polymerization of PBZ [137, 140]. Nowadays, Ran et all [140] proposed $PCl_5$ catalyst to polymerization of BZ monomer under different reaction conditions. The catalyst was observed to affect the reaction rate, temperature and solvent polarity of PBZ. They reported $PCL_5$ is highly active as catalyst for polymerization of PBZ and they dominated relatively low reaction temperature and requiring polar solvent.

Kocaarslan et al. [141] elucidated the effect of amine HCl salt catalyst for ROP of PBZ. The major effect of ammonium salt was reported it was occurred reduction reaction temperature of ROP.

Recently, the new perspective for acid catalyzed PBZ, the urushiol was reported to use as long chain hydrocarbon phenol source for ROP of PBZ by some researchers [142, 143]. Zhang et al. [142] synthesized urushiol based PBZ from urushiol, paraformaldehyde and triethylenetetramine (Figure 3.8). Then, they modified to PBZ by silane for anticorrosion coating application. The effect of silane was observed that to improve the stress of PBZ, and it may affect chemical structure of the network and the crosslink density of the network.
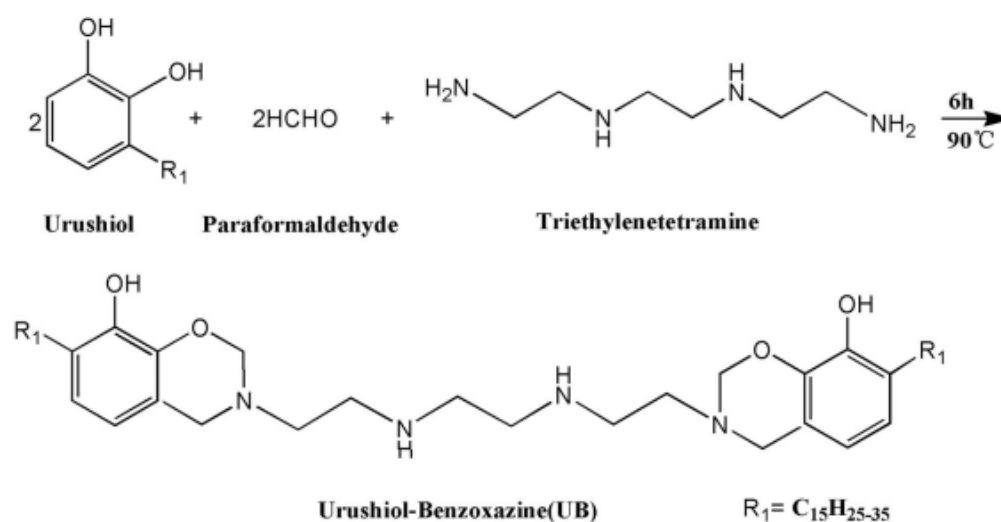


**Figure 3.8.** Synthesis of urushiol BZ [142]

Chen et al. [143] synthesized urushiol based BZ copper polymer from urushiol and n-octylamine, paraformaldehyde and $CuCl_2$ catalyst for antifouling coating application. They achieved to obtain high competent, low environmental impact PBZ for marine biofouling.

### 3.2.2.3. Photoinitiated polymerization of polybenzoxazines

Photoinitiated polymerization is a significant process for various industrial application. This process promotes the polymerization of the liquid monomer with initiated by light, naturally in the ultraviolet or visible region of the light spectrum. Photoinitiated polymerization may be classified as free radical and cationic polymerization [144, 145].

Hereafter, Kasapoglu et al. [146] studied BZ monomers of photoinitiated cationic ROP by onium salts like diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate as initiators. According to characterization result, they obtained

complex structure of PBZ because of the ROP process of the protonated monomer was interacted with the oxygen or nitrogen atoms. Also, the results showed to phenolic mechanism decreases, when the monomer concentration was decreased.

Then, the hybrid dual cure networks for PBZ through with photopolymerization and thermally accelerated cationic ROP reported by Narayanan et al. [147]. Although, the ROP mechanism was occurred in thermal ROP, in first step in polymerization was used photopolymerization method with thiol-ene based materials. They succeeded to get high Tg for thiol-ene based material (150 °C). However, the obtained PBZ network was lined up heterogeneously because of thiol and allyl functional groups outcomes from an opposing nucleophilic ROP with the radical-mediated thiol–ene photopolymerization reaction. For the future application, to obtain the well-defined networks and reduce the opposing thiol reactions will bring along settable thermal and mechanical properties.

Lately, cationic photopolymerization of BZ in aqueous solution, at room temperature, without catalyst, under UV light was reported by Salabert et al. [148]. This process is different than thermal polymerization and their obtained crosslinked network of PBZ. In this process, there is photoinduced intramolecular electron transfer between amine groups and phenyl rings. The low nucleophilicity of the nitro- or cyano-substituted phenol ring led to only onium ions continue the propagation. For ROP mechanism of PBZ, they used more electron donor substituted such as Cl, F and OMe. The photoinitiated cationic ROP could even be executed in pure water, just adding sodium dodecyl sulphate as emulsifier. The major advantage of this study is the polymerization can be occurred at room temperature and it was reported first in the literature.

### 3.3. Preparations of Blends and Composites

To prepare high-performance material, BZ based composites may be classified as (i) PBZ blends with another polymeric resin (e.g. rubber, polyurethane), (ii) composites including inorganic molecules (e.g. silica, titanium dioxide) distributed in a PBZ matrix and (iii) fibre-reinforced PBZ composites [149].

### 3.3.1. Rubber modified polybenzoxazines

To deal with intrinsic brittleness of PBZ, some of researchers investigated to modification the PBZ with rubber and their derivatives [150]. The rubber toughening

mechanism in epoxy studies showed the plastic deformation by rubber is significant as well as toughening [151-153]. There are two mechanisms for the plastic deformation made by rubber particles have been suggested: (i) shear strength of matrix between the matrix and rubber particles, and (ii) expansion of plastic gap of the matrix encircling the particle. Also, it has been indicated that the rubber particles in the matrix phase eliminate the limitation of void formation of rubber which activates the construction of shear bands [154].

Due to the difficulty of implementation of solid rubber to modify PBZ, the liquid rubber is suitable to implement to the latest phenolic polymer. Since, it is simple to process due to their low viscosity and to regulate the polarity of rubber. The way of it is changing the ratio of polybutadiene and acrylonitrile rubber. Because of distribution of rubber in matrix, the regulate of rubber polarity is significant. To improve toughening of rubber, the particle size for distribution should be around 102 – 103 nm [155].

To toughening of rubber and minimize the huge structural differences between rubber and polymer matrix, Ishida and Lee [156] used reactive rubber such modified by an amine-terminated poly (butadiene-co-acrylonitrile) rubber (ATBAN). They expected to decrease the surface tension and particle aggregation by this reactive modification with rubber participation of monomer. They obtained well-suited and uniform dispersed system with reactive rubber modified to PBZ.

Because of epoxies can be modified with core shell rubber for investigate of fracture behaviour [157], PBZ-core shell rubber–carbon nanotube nanocomposite reported by Yang et al. [158]. In this study, rubber used as nanofiller toughening agent for ternary system of PBZ. Both nanofillers were increased the fracture strength and toughness together significantly.

Caldona et al. [159] have been prepared a nanocomposite with rubber modified PBZ and silica ($SiO_2$). They used hydroxyl-terminated BZ monomer and as a toughening modifier epoxidized polybutadiene (HTBD) due to their reactivity with the hydroxyl groups formed ROP of BZ and thereby may crosslink the PBZ matrix. To prepare superhydrophobic nanocoating, they utilized with $SiO_2$ because of their behavior about surface roughness decrease. They obtained a superhydrophobic and super oleophilic nanocomposite for various applications.

Another anti corrosion application with rubber modified PBZ reported by Caldona et al. [160]. They prepared a composite with hydroxyl terminated epoxidized polybutadiene modified PBZ and different loadings of polyaniline emeraldine salt (PANI ES) filler. The PBZ-PANI composite anti corrosion coating for carbon steel was succeeded with dosage of 0.50% by weight PANI. Caldona et al. [161] prepared another anti corrosion nanocomposite coating with rubber modified PBZ and graphene oxide to improve the barrier performance and corrosion resistance of carbon steel.

### 3.3.2. Polycarbonate blends with polybenzoxazine

Brittleness of PBZ come from their crosslinking system can be tolerated with modification or blending system with another substituents. To better toughness of PBZ, another way is preparing a blend with polycarbonate (PC). PC blends with PBZ reported by Ishida and Lee [162]. They observed the hydrogen bond occurred between hydroxyl group from PBZ and carbonyl group from PC. Also, they investigated the PC provided slow ROP at beginning of curing stage to PBZ, that is give thermal stability and toughness. In the next study of Ishida about PBZ-PC blend system, the transesterification reaction with ROP was reported [163]. The transesterification provides the replacement of hydroxyl groups to the phenolic chain ends of the PC from BZ mainchain and it may better ROP for PBZ. However, providing shear the long chain of PC into short segments causes poor thermal properties for blend system.

### 3.3.3. Poly(epsilon-caprolactone) blends with polybenzoxazine

Thermally stable poly(e-caprolactone) (PCL) due to their low Tg, is good application to modify the PBZ. Ishida and Lee [164, 165] prepared a blend with PBZ and PCL due to take advantage of toughness PCL. They observed high thermal stability because of high melting temperature of PCL and they need low temperature to curing without use any solvent. The crosslinking increases with increase the content of PCL, however the addition of more PCL attributed to more molecular sections.

Regarding miscibility of blend of PBZ-PCL some studies were reported [166, 167]. Because of the lower molecular weight of the BZ monomer, the miscibility of the blend attributed to the share of entropy to the fluxing free energy.

From the view point of dielectric constant of PBZ-PCL blend, Su et al. [168] prepared porous material with low dielectric value. As previous studies, the hydrogen bond

between hydroxyl groups from PBZ and carbonyl groups from PCL is significant for miscibility of blend or copolymer of PBZ-PCL. They modified end group of PCL to reduce the degree of phase separation.

The diblock copolymer poly(ethylene oxide-b-e-caprolactone) (PEO-b-PCL) with the monomer (3-phenyl-3,4-dihydro-2H-1,3-benzoxazin-6-yl)methanol (PA-OH) blend reported by Chu et al. [169]. This study showed the PA-OH and PEO intermolecular hydrogen bonding is stronger than between the PA-OH and PCL hydrogen bond in the PBZ blend system. Nevertheless, to obtain high Tg, should be add more PCL than 20 wt%, that cause corruption the processability and hard miscibility because of the adding high molecular weight.

Latest, the toughening of PBZ the covalent and non-covalent bonding of PCL within BZ monomer, preparing the copolymer and blend were reported by Schäfer and Koschek [170]. They compared composition of component and interaction bonding. Therefore, they obtained the most effective synthesize system for toughening PBZ reported as covalent bonding type of 10-20 wt. % PCL addition.

### 3.3.4. Polyurethane (PU) blends with polybenzoxazine

Another possible modifier for PBZ is polyurethane (PU) because of their ultimate advantages like easy processability, flexibility in low temperature, resistance to oil and abrasion. In addition, they have not only had properties from plastics but also from rubbers properties in it because they classified as elastomer [171, 172]. Beside these advantages, they have some handicaps like low thermal stability and poor resistance against polar structure. Regarding the study which had been reported by Masiulanis et al. [173] thermal durability and thermal degradation temperature are 80-90 °C and 200 °C respectively. The PBZ-PU blend occurs between the hydroxyl groups from PBZ and -NCO groups from PU interaction [174].

Alternatively, Takeichi, Guo and Agag [175] prepared the blend with PU prepolymer-phenolic resin and BZ monomer. They used thermal treatment for curing the PU-BZ film in THF. They obtained great resistance to organic solvents and improved thermal stability compared with components of blend.

Cui et al. [176] synthesized ordinal interpenetrating polymer networks (IPNs), with PU-PBZ blend. According to characterization results, in resulting IPNs have only

physical bond, so on it is understood that there is no evident graft reaction among the PU-PBZ blend through the construction of IPN.

Li et al. [177] prepared poly(benzoxazine-co-urethane) by melt blending with bisphenol-S/aniline-type BZ (BS-a) with isocyanate-accelerated PU prepolymer based on 2,4-toluene diisocyanate and poly (ethylene glycol). The blend was prepared by thermally activated ROP. The adjustments in the ratio of BS-a/PU prepolymer induce morphological changes and cause to be difference in dynamic mechanical possessions, thermal stability of blend and water absorption.

New perspective for PU-PBZ blend was prepared as biobased hydroxyl functional BZ monomer synthesized from Guaiacol (lignin derivative) by thermal ROP method and absence of solvent [178]. The blend coating was prepared for corrosion resistant on mild steel. They obtained increases PU content, increase the corrosion resistant behavior of blend.

### 3.3.5. Epoxy blends with polybenzoxazine

The blending of epoxy with PBZ network is used for toughening and crosslinking therefore improve the mechanical and thermomechanical properties of PBZ. Thermomechanical improvement of PBZ was investigated by Rimdusit et al. [179] They used arylamine based BZ resin to prepare an allow with BZ and epoxy. The bisphenol A-based epoxy was used as crosslinkers to improve thermal and mechanical properties of blend system. The phase separation of BZ-epoxy blend was investigated [180]. They compared the polymerization of BZ and epoxy separately and the polymerization of mixture. They observed the mixture polymerization was more complex due to ROP of BZ resin and homo polymerization or copolymer of epoxy resin. The significant point of their characterization result showed the polymerization sequence influenced the phase separation of blend system. In contrast, Wang et al. [181] synthesized hyperbranched polyether epoxy reinforced BZ to avoid the phase separation. They aimed to show the improvement of the toughness without reducing other properties of the PBZ resin. Other studies about hyperbranched polymeric ionic liquid [182] and hyperbranched polyether epoxy [183] were investigated for toughness, mechanical and thermal properties of PBZ-epoxy blend system.

Abed et al. [184] investigated effect of fumes silica on properties of composite of PBZ-Epoxy. They illustrated the increases of fumed silica increase the thermal stability of

PBZ composite. Regarding characterization result, they decided the fumed silica weigh ratio as 4% for exposed higher tensile and flexural strength.

Another perspective about the subject of epoxy and PBZ was investigated by Su et al. [185]. They prepared a blend with epoxy and poly (ethylene oxide–b–ε-caprolactone) (PEO-b-PCL) di block copolymer together with BZ monomer as thermal curing agent. Regarding SEM result, structural shape of epoxy-BZ matrix and PEO-b-PCL copolymer dispersed phase bring the ultimate toughness.

Recently, Musa et al. [186] studied different weight ratios BZ monomer modified with epoxy resin to observe coating performance and thermal properties of blend. They succeeded to prepare hydrophobic coating with 20% weigh ratio of BZ monomer modified with epoxy.

### 3.3.6. Phosphorous containing blends with polybenzoxazines

Phosphorus is used for bring flame retardant property to PBZ due to delaying polymer ignition is to inhibit the fuel source by enclosing the investment of the material with a non-flammable coating. Two different ways were recommended to prepare the flame retardant PBZ by Espinoza et al. [187, 188]. First one is using BZ-glycidyl phosphinate copolymer to modify the novalac resin. Second is curing BZ with isobutyl bis(glycidylpropylether) phophine oxide for modified novalac resins.

Another research about obtaining flame retardant PBZ investigated by Lin et al. [189]. They examined the subject within three methods such as; (1) prepare a blend with phosphorous containing triphenol (dopotriol) BZ and [6,6-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazineyl) methane (F-a)] or diglycidyl ether of bisphenol A (DGEAB), (2) the phosphorous element was involved into BZ through curing reaction with same materials of first method, (3) dopo reacted with BZ to include the phosphorous.

Sponton et al. [190] used silicon together with phosphorous element to get flame retardant PBZ-epoxy blend because of utilize the property of silicon establishing thermally stable silica. Herewith, the blend has disposition to move to the char surface providing as a defense layer to avoid more degradation of char at high temperatures. They synthesized diglycidyl ether of (2,5-dihydroxyphenyl) diphenyl phosphine oxide (Gly-P) and diglycidyloxymethylphenylsilane (Gly-Si). They observed the phosphorus-containing materials because of high limiting oxygen index (LOI) values show excellent flame-retardant properties in contrast of silicon containing materials.

Another BZ-epoxy copolymer with containing phosphorous element to prepare flame retardant PBZ reported by Peng et al. [191]. In this study BZ used as curing agent to develop the thermal stability and oxidative stability of epoxy. They aimed and succeeded to prepare compatible epoxy-BZ copolymer with liquid oxygen (LOX) for LOX tank.

### 3.3.7. Clay-PBZ composites

To prepare organic and inorganic nanocomposites clays are potential candidates due to they may be divided into nanoscale building blocks and make supporting phase in hybrid nanocomposites [192]. In addition, they are low-cost fillers for polymers and they have skill to improve the final materials.

Agag et al. [193] prepared a hybrid nanocomposite with PBZ and organically modified montmorillonite (OMMT) as a sort of layered silicates. They observed the curing temperature of nanocomposite was lower than pristine BZ and OMMT in contrast thermal stability of nanocomposite was high. There is another perspective to preparing PBZ-clay nanocomposite addition with polyurethane reported by Takeichi and Guo [194]. OMMT act as catalytic effect to hybrid PU-PBZ nanocomposite and decrease the curing temperature like previous study. The hybrid nanocomposite showed ultimate solvent resistance and thermal stability with small amount of OMMT. Phiriyawirut et al. [195] aimed to improve the OMMT quality for better hybrid nanocomposite such as exchange capability, polarity of the organic ion or respectability, polarity of solvent, and chemistry of organic ion on the separation of silicate layers. Chen et al. [196] prepared a hybrid nanocomposite with PBZ-OMMT in addition bisoxazoline (2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles).

S.M. El-Mesallamy [197] prepared a hybrid nanocomposite with PBZ-clay for metal coating. He used OMMT and bis-(3-dodecyel-3,4-dihydro-2H-1,3-benzoxazine) isopropane (B-dod) to prepare the PBZ-clay nanocomposite and OMMT was prepared via modification of sodium montmorillonite (Na-MMT) with different ammonium salts of amines such as tyramine (Tyr), amino lauric acid (ALA) and N,N-dimethyl stearyl amine (DMS). According to characterization results, the exfoliation of organoclay into BZ matrix was completed with 20 wt. % of organoclay. The existence of BZ in the organoclay interlayers interrupts the aggregation of layers of clay. He obtained mechanically improved, thermally stable hybrid nanocomposite.

Lately, Alhwaige et al. [198] prepared composite aerogels with chitosan/PBZ/clay by freeze-drying of different Na-MMT colloidal distributions. In this study Na-MMT was bring greater thermal stability to the chitosan/PBZ/clay composite through it was developed the onset decomposition temperatures. Due to the thermal ROP of BZ, the polymerized aerogels are extremely stable in neutral water and in acidic medium.

## 4. EPDM-POLYBENZOXAZINE (PBZ) BLENDS

### 4.1. Materials

Polybenzoxazine was synthesized from 4-Hydroxybenzaldehyde (98%), 2-(Trifluoromethyl)aniline (98%) and paraformaldehyde, and it was catalyzed with 2 (Dimethylamino)-ethanol (DMAE) (99+%). 4-Hydroxybenzaldehyde (98%) and paraformaldehyde were used from Aldrich Chemistry, 2-(Trifluoromethyl)aniline (98%) and 2-(Dimethylamino)-ethanol (DMAE) (99+%) was purchased from Alfa Easer. EPDM (Royalene 525) was used to prepared a blend with PBZ. It was purchased from Sigma Aldrich. Nano $TiO_2$ was used as additive for prepare a polymer nanocomposite with PBZ-EPDM. It was obtained from Sigma Aldrich. Another additive for PBZ-EPDM nanocomposite was PTFE. PTFE was purchased from Sigma Aldrich. To crosslink the EPDM, it was used sulfur. Sulfur was purchased from Sigma Aldrich.

### 4.2. Methods

To synthesize PBZ, the mixture tube was stirred with magnetic stirrers and placed on hot plate oil bath as shown in Figure 4.1.
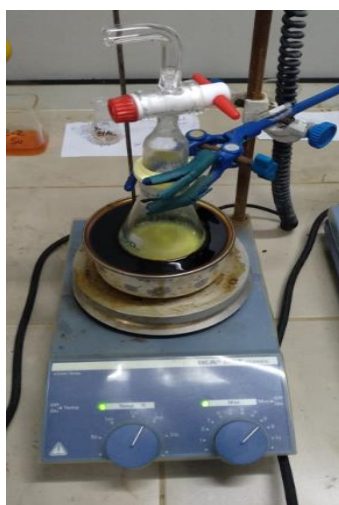


**Figure 4.1.** The mixture of polymer in oil bath on hot plate magnetic stirrers

To characterize hydrophobic properties of the PBZE1-EPDM nanocomposite, it was used drop shape analyzer. The contact angle measurements were obtained from Krüss drop shape analyzer as shown in Figure 4.2.
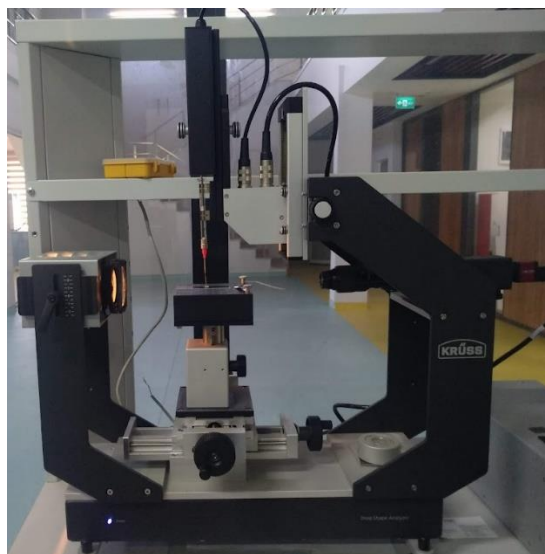


**Figure 4.2.** Drop Shape Analyzer for contact angle measurements

Fourier-transform infrared (FTIR) spectra of KBr disks were obtained using a Perkin Elmer FT IR Spectrometer Spectrum Two as Figure 4.3.



**Figure 4.3.** FTIR Spectrophotometer

The optical properties of the nanocomposite samples were characterized with UV-Vis Spectrophotometer (Shimadzu, UV-2600) (Figure 4.4).

**Figure 4.4.** UV-Vis. Analyzer

The Cressington 108auto Sputter Coater (Figure 4.5) is used principally for sputtering conducting gold layers onto polymer samples to prevent charging effects in the scanning electron microscope (SEM).



**Figure 4.5.** Coater for polymer samples to take SEM image

For thermal characterization, it was used NETZSCH STA 449F1 brand thermogravimetric analysis (TGA) device. The samples were prepared at 10 °C/min. from room temperature to 800 °C according to ASTM D6370 standard. % mass loss was analyzed by testing in nitrogen environment with temperature increase.

## 4.3. Results

### 4.3.1. Synthesis of PBZ polymer (PBZE1)

Into 250mL round flask were added 4- Hydroxybenzaldehyde (5 g, 40 mmol), 2-(Trifluoromethyl)aniline (6 mL, 40 mmol), paraformaldehyde (6 g, 200 mmol) and DMAE (5 mL). DMAE was used as base catalyst. The mixture was stirred and placed in 100 °C, oil bath for 24 hours after the tube was closed with vacuum pump. After 24 hours and cooled the room temperature, it was obtained light yellow, tough and brittle PBZ polymer (Figure 4.6) [200]. The efficiency was measured as 78,8139 %. The synthesis reaction for PBZE1 as shown in Figure 4.7.



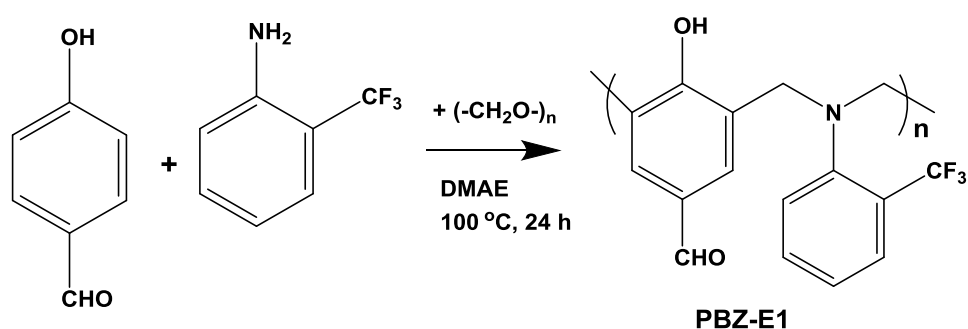**Figure 4.6.** The obtained solid PBZ polymer after decontamination step



**Figure 4.7.** Synthesis reaction of PBZE1 [199-201]

For decontamination, it was purified with distilled water (50 mL) and dried up in oven for 5 hours in 100 °C.  In addition, it was observed the PBZE1 polymer can be dissolve in ethyl acetate. It was occurred colloidal balls in one phase when we added stirred

with distilled water and showed surfactant behavior. The pH value of PBZE1 was reported as approximately 12.

The molecular weight of PBZE1 was measured with Gel permeation chromatography (GPC) and shown in the Figure 4.8. [201]. In the Figure 4.8; Mn is 28.788, Mw is 71.644 and Mw/Mn is 2.489.
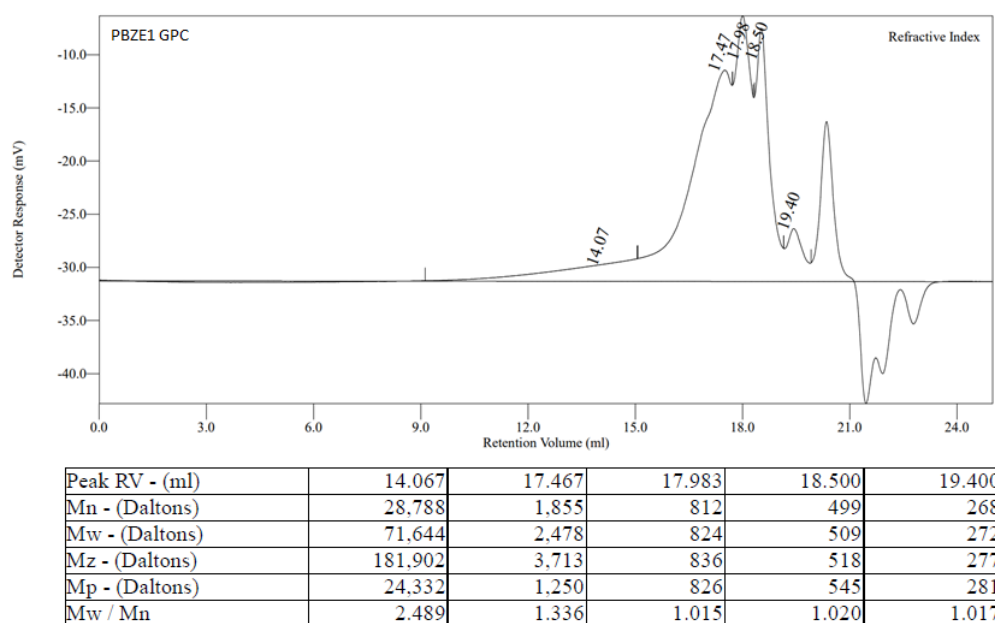


| Peak RV - (ml) | 14.067 | 17.467 | 17.983 | 18.500 | 19.400 |
|---|---|---|---|---|---|
| Mn - (Daltons) | 28,788 | 1,855 | 812 | 499 | 268 |
| Mw - (Daltons) | 71,644 | 2,478 | 824 | 509 | 272 |
| Mz - (Daltons) | 181,902 | 3,713 | 836 | 518 | 277 |
| Mp - (Daltons) | 24,332 | 1,250 | 826 | 545 | 281 |
| Mw / Mn | 2.489 | 1.336 | 1.015 | 1.020 | 1.017 |

**Figure 4.8.** GPC measurement results for PBZE1 polymer [201]

### 4.3.2. Preparation PBZE1-EPDM nanocomposite filled by nano $TiO_2$ and PTFE

The blend was prepared with PBZE1 (0,5690 gr) and EPDM (0,5690 gr/20 mL $CHCl_3$), because of increase the elasticity of the PBZE1. Then it was added nano $TiO_2$ (0,1422 gr), PTFE (0,1422 gr) and stirred up mechanically to prepare the nanocomposite. The weigh ratios were recorded as 40 %(PBZE1), 40% (EPDM), 10% (nano $TiO_2$) and 10% (PTFE) respectively. To prepare the PBZE1-EPDM-PTFE-Nano $TiO_2$ polymer nanocomposite with sulfur, it was added 0,015 gr sulfur (0,1 % weigh ratio) and stirred again mechanically.

In the Figure 4.9, it was illustrated the PBZE1-EPDM-PTFE-Nano $TiO_2$ polymer nanocomposite.
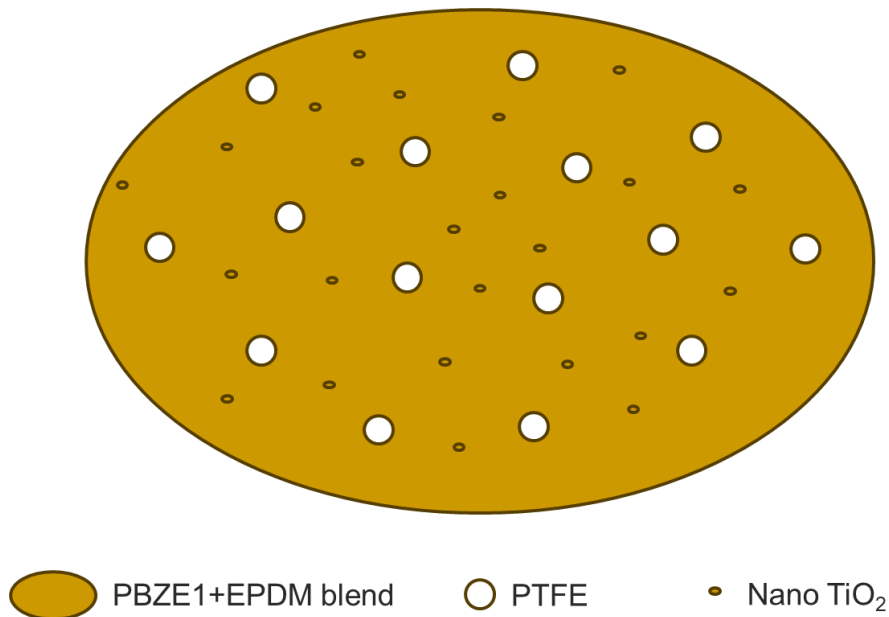
**Figure 4.9.** The illustration of PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite

### 4.3.3. Vulcanization and curing

To crosslink the PBZE1-EPDM polymer nanocomposite, it was added sulfur and prepared at 25 °C and vulcanized at 100 °C, 150 °C and 180 °C respectively. The other PBZE1-EPDM polymer nanocomposite samples without sulfur were prepared at the same temperatures. The samples were called according to their components as follow;

• PBZE1-EPDM-PTFE-Nano TiO$_2$: The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared without sulfur at 25 °C.

• PBZE1-EPDM-PTFE-Nano TiO$_2$-100: The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared without sulfur at 100 °C.

• PBZE1-EPDM-PTFE-Nano TiO$_2$-150: The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared without sulfur at 150 °C.

• PBZE1-EPDM-PTFE-Nano TiO$_2$-180: The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared without sulfur at 180 °C.

• PBZE1-EPDM-PTFE-Nano TiO$_2$-S: The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared with sulfur vulcanized at 25 °C.

• PBZE1-EPDM-PTFE-Nano TiO$_2$-S-100: The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared with sulfur vulcanized at 100 °C.

- PBZE1-EPDM-PTFE-Nano TiO$_2$-S-150: The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared with sulfur vulcanized at 150 °C.

- PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was prepared with sulfur vulcanized at 180 °C.

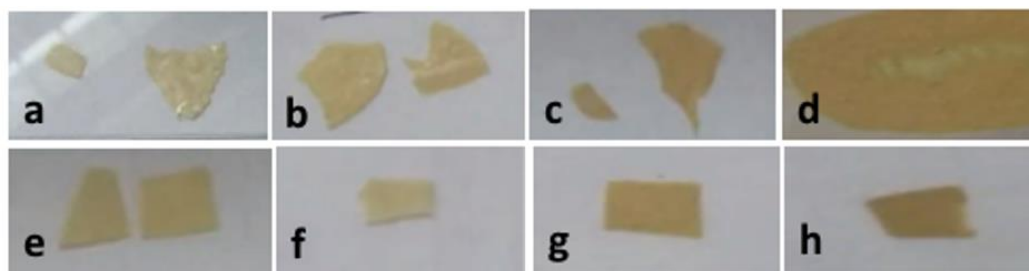The picture of all of the sample is as shown in Figure 4.10.



**Figure 4.10.** a) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$, b) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$-100, c) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$-150, d) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$-180, e) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S, f) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-100, g) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-150, h) Image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180

### 4.3.4. Characterization

In this study, it was aimed to prepare hydrophobic nanocomposite with polybenzoxazine and ethylene propylene diene monomer rubber filled with titanium dioxide and polytetrafluoroethylene. Besides PBZs are hydrophobic materials, it was chosen fluorine in synthesizing step of PBZ. The PBZ should not be solved in water, on the contrary it should push the water, to be hydrophobic material. Thus, it was taken help from fluorine, to be more hydrophobic. To improve the hydrophobic property, another applied is preparing the blend with EPDM rubber and chosen hydrophobic filler material. So, nano TiO$_2$ and PTFE are being help to improve hydrophobic properties of the polymer nanocomposite. With all these assistances, it was envisaged that materials with high hydrophobicity could be prepared.

To investigate surface properties of PBZ-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite samples, SEM images were taken. In Figure 4.11, it can be seen SEM image of neat PBZE1 polymer.
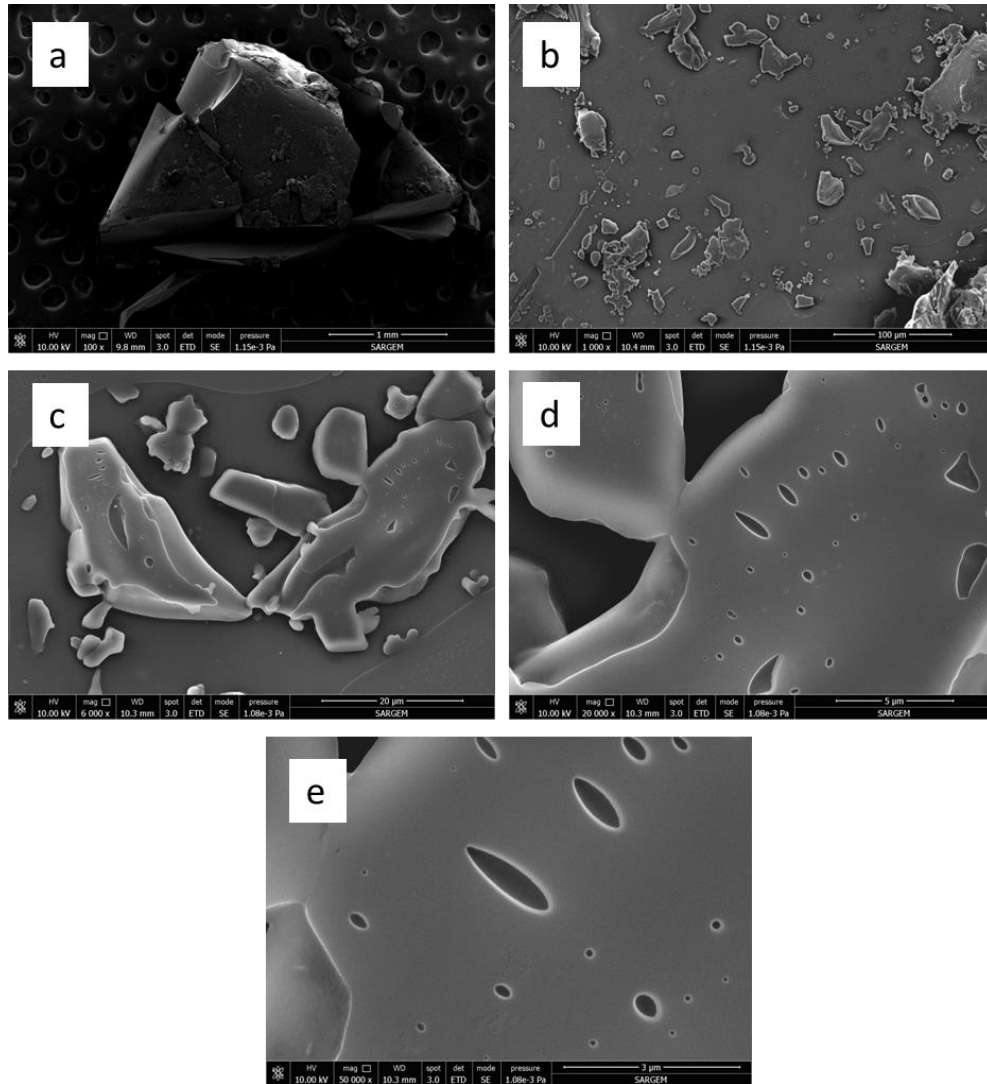
**Figure 4.11.** SEM images of neat PBZE1 polymer zoomed a) 100x times b) 1000x times c) 6000x times d) 20000x times e)50000x times

In the Figure 4.12, it can be seen SEM images of PBZE1-EPDM-PTFE-Nano TiO$_2$. It can be seen the distribution of particles on as the image zoomed. (Figure 4.12.e)

**Figure 4.12.** SEM images of PBZE1-EPDM-PTFE-Nano TiO$_2$ zoomed a) 100x times b) 1000x times c) 6000x times d) 20000x times e)50000x times

The SEM image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S polymer nanocomposite sample is given below. (Figure 4.13).



**Figure 4.13.** SEM image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S polymer nanocomposite sample

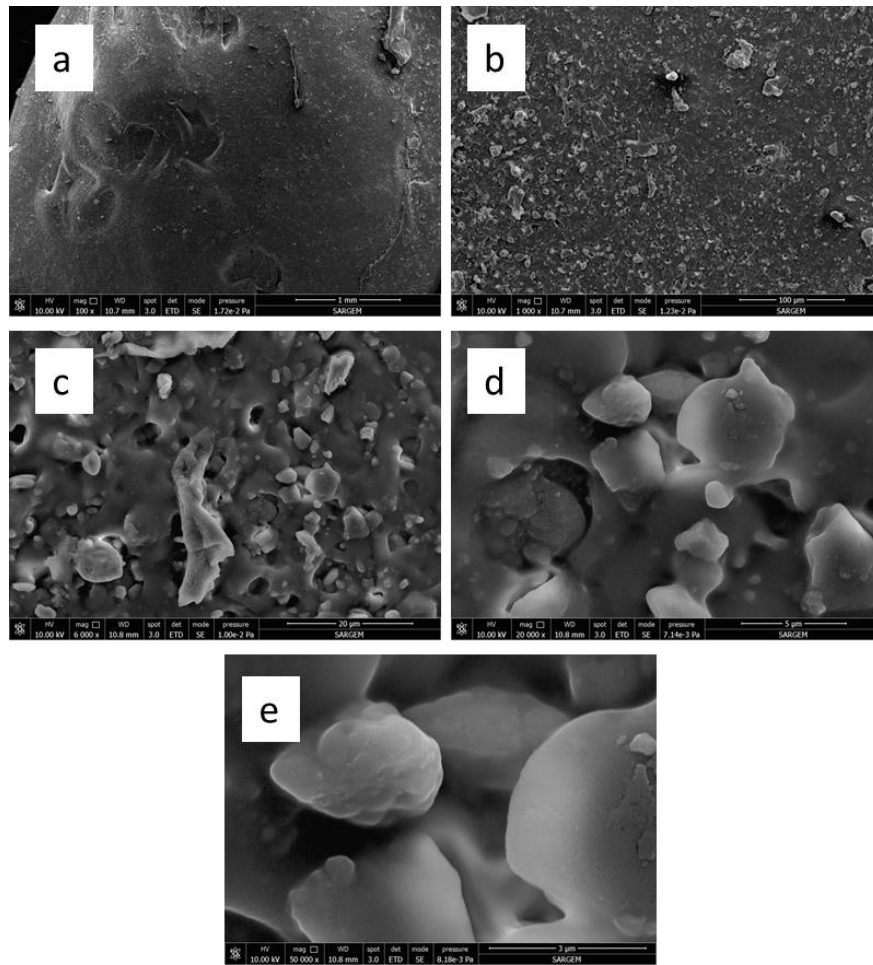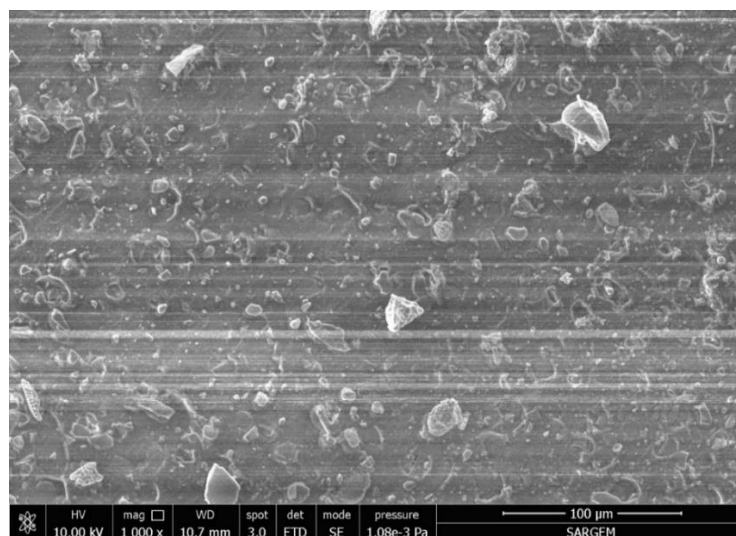SEM images of PBZE1-EPDM-PTFE-Nano $TiO_2$-150 are shown as Figure 4.14.



**Figure 4.14.** SEM image of PBZE1-EPDM-PTFE-Nano $TiO_2$-150 zoomed a) 100x times b) 1000x times c) 6000x times d) 20000x times e)50000x times

The SEM image of PBZE1-EPDM-PTFE-Nano $TiO_2$-S-180 polymer nanocomposite sample as in the Figure 4.15. There are some holes in the surface as it can be seen in the Figure 4.15. It can be said the holes came from formaldehyde. At the high temperature, formaldehyde can be volatile and it causes to holes at the surface of the polymer nanocomposite film.
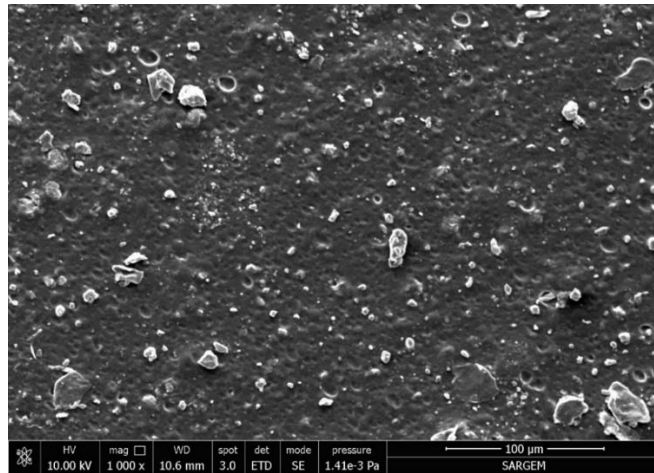
**Figure 4.15.** SEM image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer nanocomposite sample

The SEM images of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer nanocomposite samples are given below. (Figure 4.16). It can be seen the holes more clearly as gets zoomed. In the Figure 4.16.e, there are some cracks at the surface may be caused from high temperature.
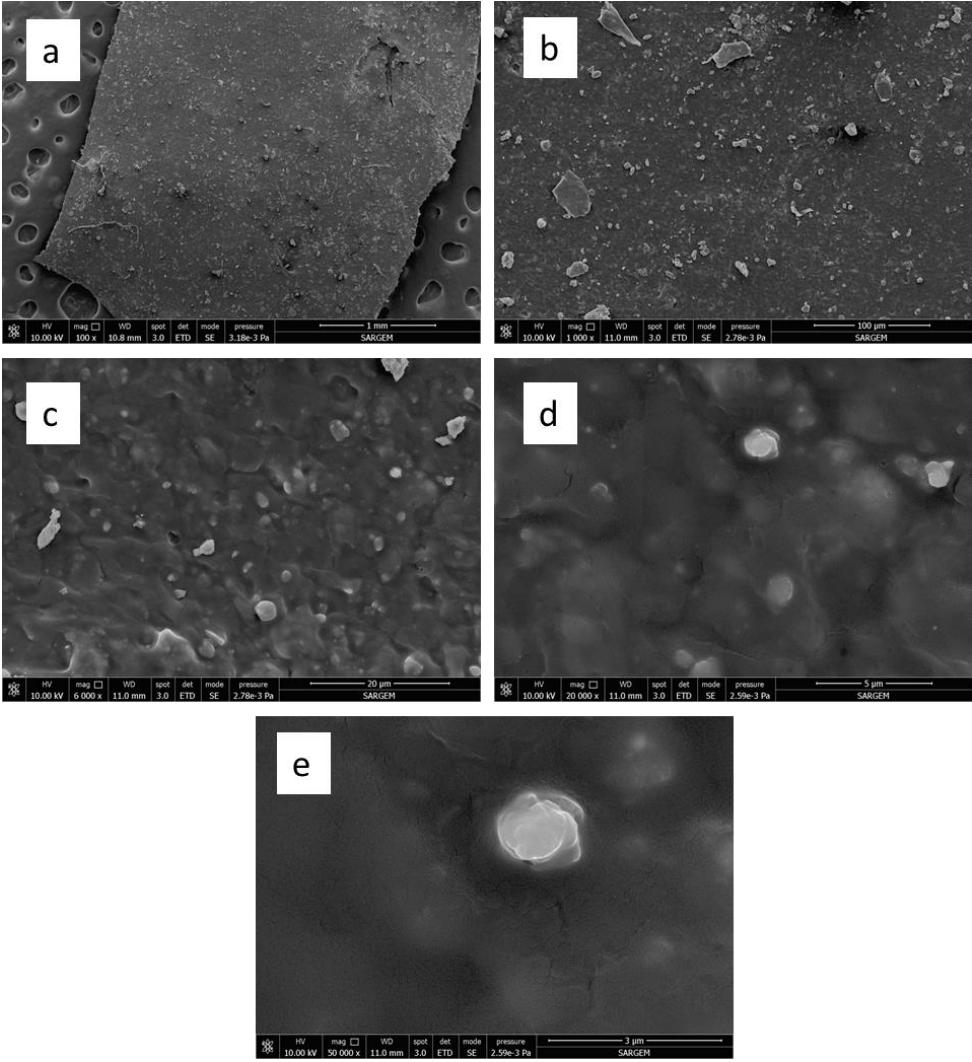


**Figure 4.16.** SEM image of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 zoomed a) 100x times b) 1000x times c) 6000x times d) 20000x times e)50000x times

The SEM-EDX results for PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite sample, elemental analysis and ratio of elements are shown in Figure 4.17, Figure 4.18 and Table 4.1.



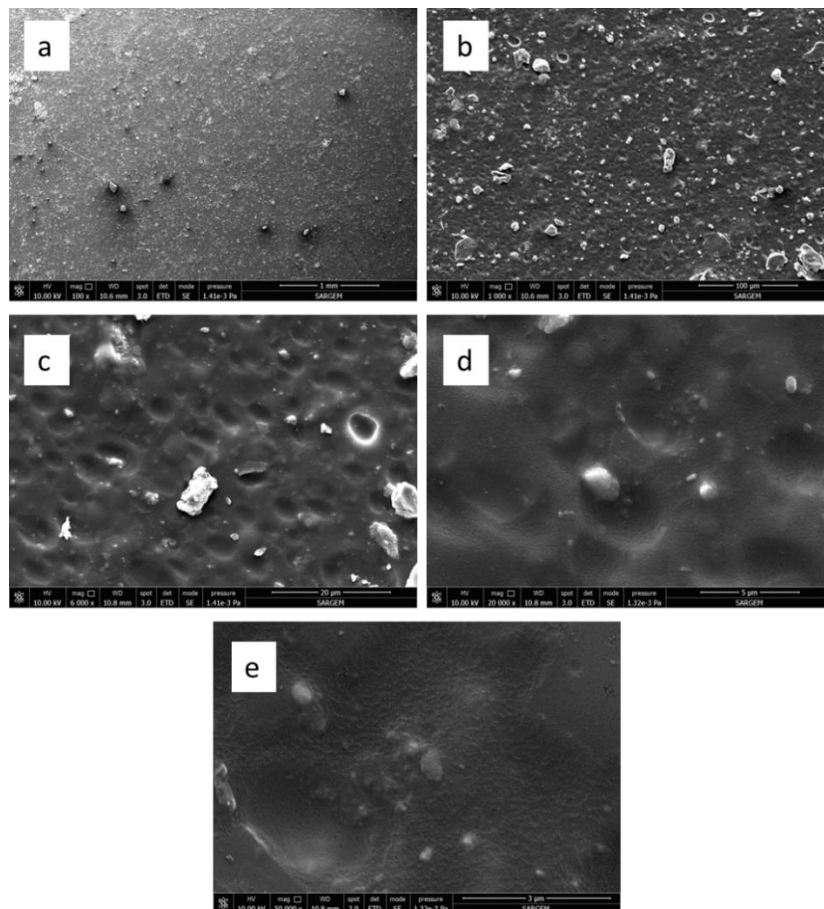**Figure 4.17.** For PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite sample a) SEM image b) SEM-EDX and O, Ti element respectively



Lsec: 18.7 0 Cnts 0.000 keV Det: Octane Plus Det

**Figure 4.18.** EDX spectrum elemental analysis for PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite sample

**Table 4.1.** EDX spectrum elemental analysis values for PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite sample

| Element | Weight % | Atomic % | Net Int. |
|---------|----------|----------|----------|
| O K | 29.95 | 56.14 | 106.25 |
| Ti K | 70.05 | 43.86 | 186.00 |

The SEM-EDX results for PBZE1-EPDM-PTFE-Nano TiO$_2$-150 polymer nanocomposite sample, elemental analysis and ratio of elements are shown in Figure 4.19, Figure 4.20 and Table 4.2.



**Figure 4.19.** For PBZE1-EPDM-PTFE-Nano TiO$_2$-150 polymer nanocomposite sample a) SEM image b) SEM-EDX and C, N, O, Ti element respectively



Lsec: 18.9 0 Cnts 0.000 keV Det: Octane Plus Det

**Figure 4.20.** EDX spectrum elemental analysis for PBZE1-EPDM-PTFE-Nano TiO$_2$-150 polymer nanocomposite sample

**Table 4.2.** EDX spectrum elemental analysis values for PBZE1-EPDM-PTFE-Nano TiO$_2$-150 polymer nanocomposite sample

| Element | Weight % | Atomic % | Net Int. |
|---------|----------|----------|----------|
| C K | 3.70 | 8.22 | 24.54 |
| N K | 2.80 | 5.33 | 17.43 |
| O K | 30.87 | 51.52 | 119.38 |
| Ti K | 62.64 | 34.92 | 177.44 |

The SEM-EDX results for PBZE1-EPDM-PTFE-Nano TiO$_2$-S polymer nanocomposite sample, elemental analysis and ratio of elements are shown in Figure 4.21, Figure 4.22 and Table 4.3.
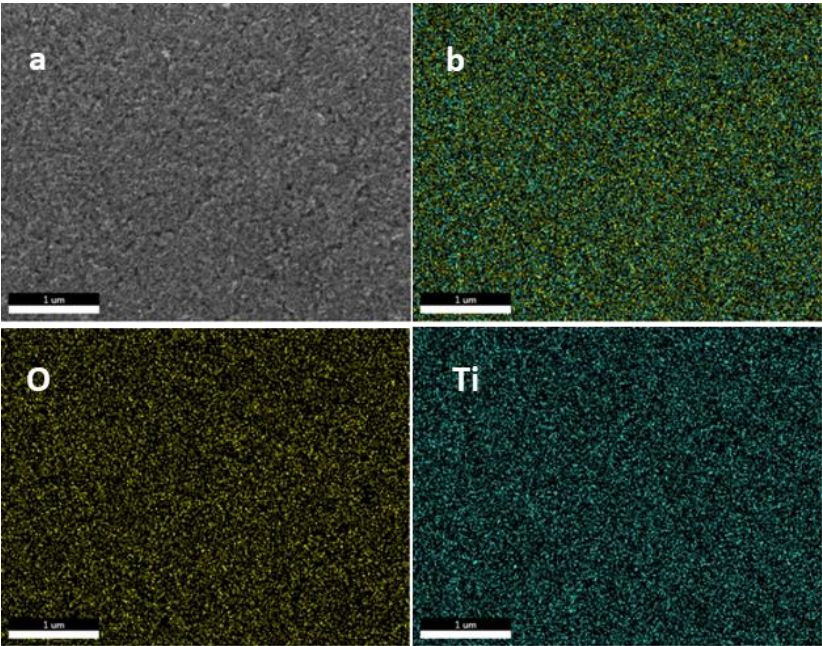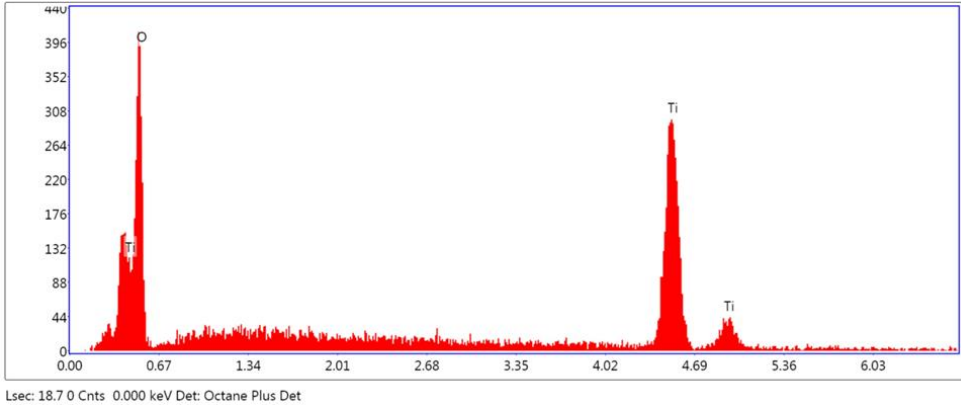


**Figure 4.21.** For PBZE1-EPDM-PTFE-Nano TiO$_2$-S polymer nanocomposite sample
a) SEM image b) SEM-EDX and C, N, O, Ti element respectively



Lsec: 18.6 0 Cnts  0.000 keV Det: Octane Plus Det

**Figure 4.22.** EDX spectrum elemental analysis for PBZE1-EPDM-PTFE-Nano TiO$_2$-S polymer nanocomposite sample

**Table 4.3.** EDX spectrum elemental analysis values for PBZE1-EPDM-PTFE-Nano TiO$_2$-S polymer nanocomposite sample

| Element | Weight % | Atomic % | Net Int. |
|---------|----------|----------|----------|
| C K | 5.87 | 12.50 | 39.94 |
| N K | 2.85 | 5.21 | 16.95 |
| O K | 31.53 | 50.40 | 126.31 |
| TiK | 59.75 | 31.90 | 171.01 |

The SEM-EDX results for PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer nanocomposite sample, elemental analysis and ratio of elements are shown in Figure 4.23, Figure 4.24 and Table 4.4.
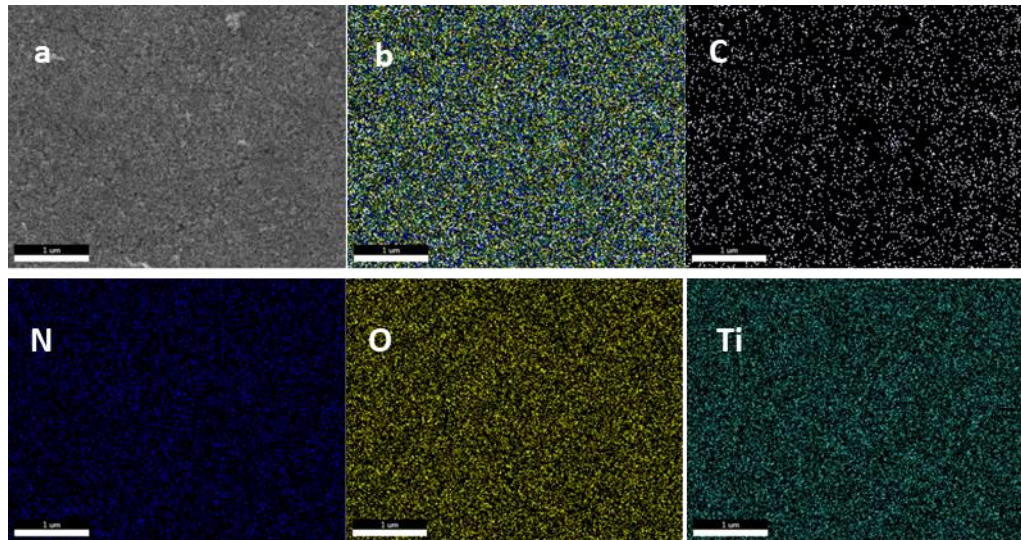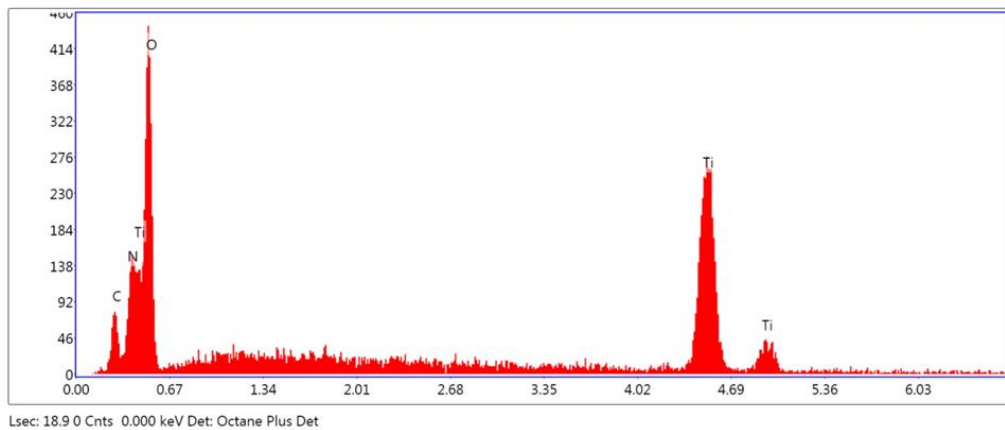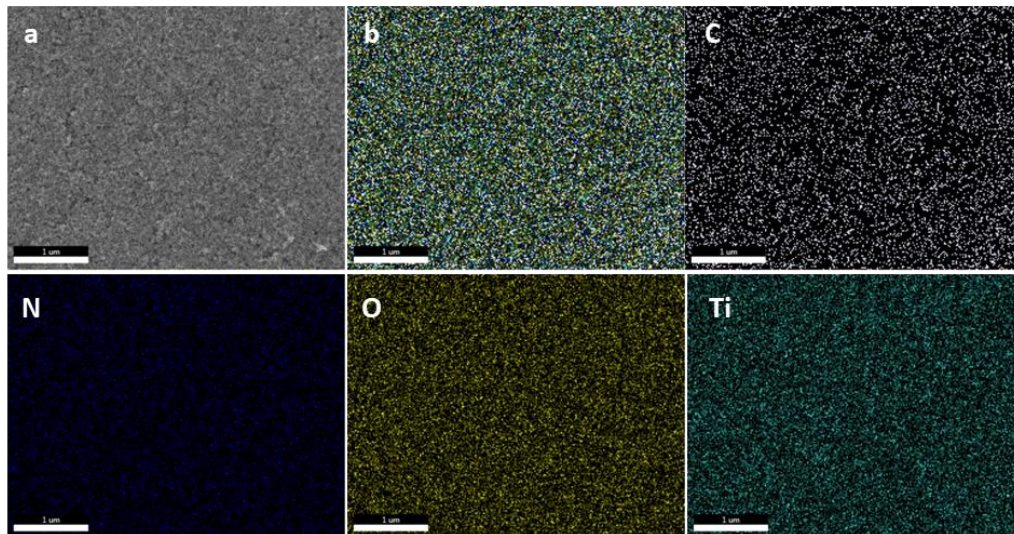


**Figure 4.23.** For PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer nanocomposite sample a) SEM image b) SEM-EDX and C, N, O, S, Ti element respectively



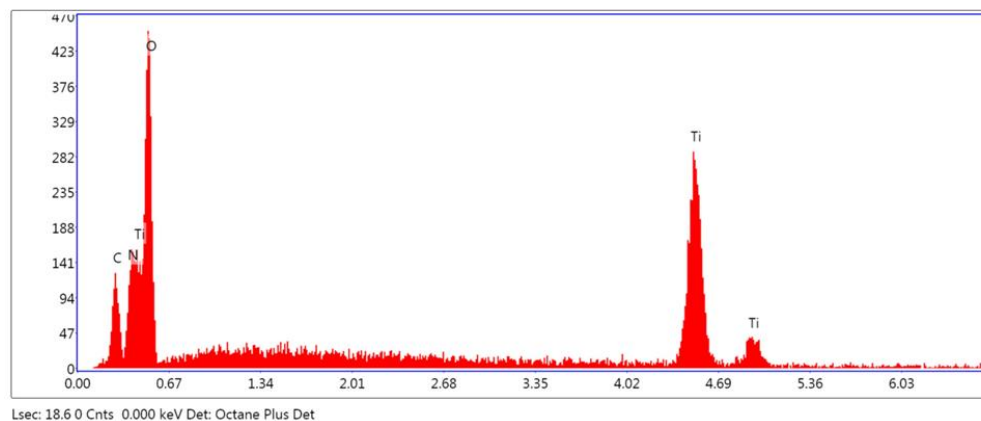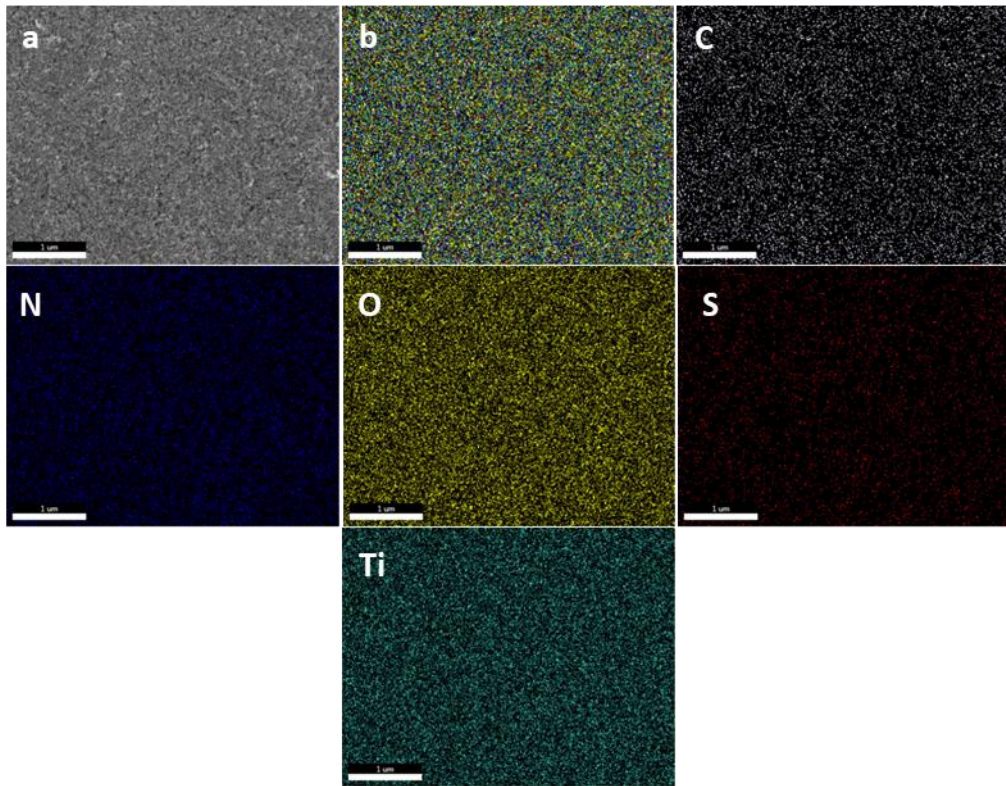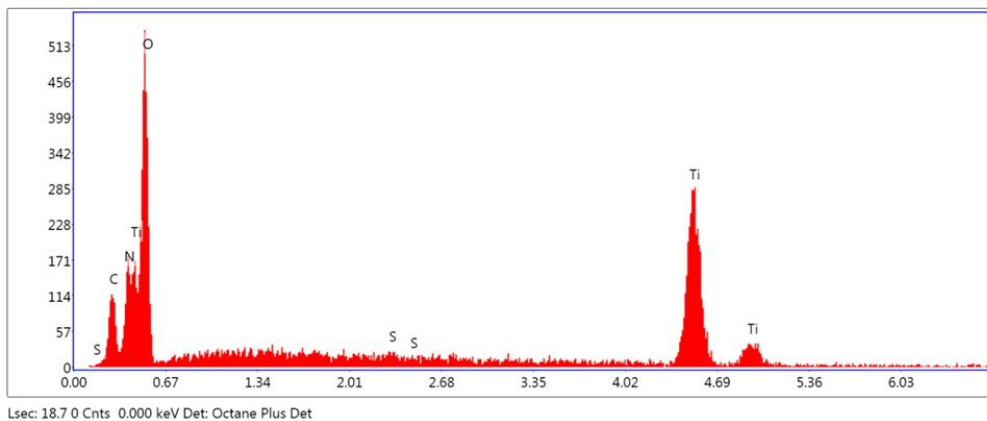Lsec: 18.7 0 Cnts  0.000 keV Det: Octane Plus Det

**Figure 4.24.** EDX spectrum elemental analysis for PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer nanocomposite sample

**Table 4.4.** EDX spectrum elemental analysis values for PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer nanocomposite sample

| Element | Weight % | Atomic % | Net Int. |
|---------|----------|----------|----------|
| C K | 5.37 | 11.37 | 36.24 |
| N K | 2.89 | 5.24 | 17.52 |
| O K | 32.67 | 51.90 | 135.58 |
| S K | 0.55 | 0.44 | 5.78 |
| TiK | 58.51 | 31.05 | 170.33 |

The contact angle measurements were analyzed as shown in Figure 4.25. The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite without sulfur prepared at room temperature (Figure 4.25 (a)) does not show hydrophobic properties, because of the contact angle measurement was reported as approximately 62°. However, the same PBZE1-EPDM-PTFE-Nano TiO$_2$ nanocomposite sample treated at 180 °C (Figure 4.25 (c)) was showed hydrophobicity. The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite sample in the presence of sulfur was attained as hydrophobic, even if wasn't applied vulcanization temperature as shown in Figure 4.25 (b). As a result of the contact angle was measured as 101,1°, it can be seen the most hydrophobic PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposites were obtained in the existence of sulfur vulcanized at 180 °C (Figure 4.25 (d)).
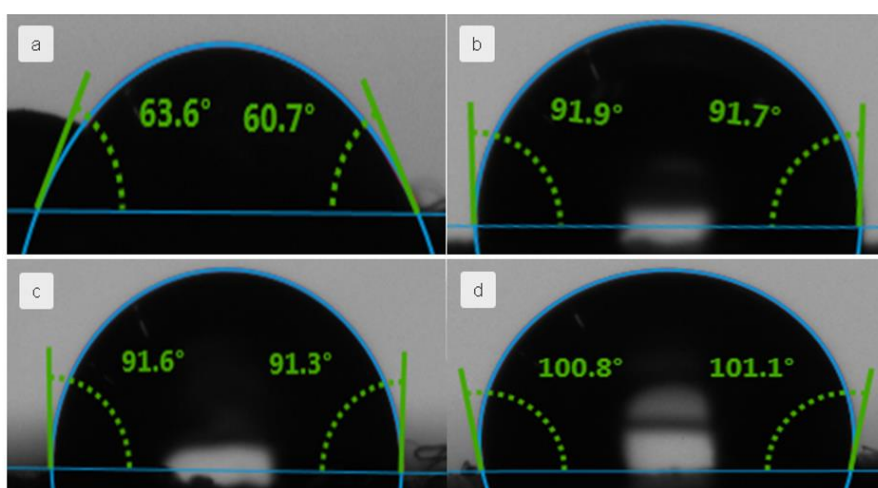


**Figure 4.25.** Image of contact angle measurements of PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite samples; a) PBZE1-EPDM-PTFE-Nano TiO$_2$, b) PBZE1-EPDM-PTFE-Nano TiO$_2$-S, c) PBZE1-EPDM-PTFE-Nano TiO$_2$-180, d) PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180

The optical properties of PBZE1-EPDM-PTFE-Nano $TiO_2$ nanocomposite samples were characterized with UV-Vis Spectrophotometer. The polymer nanocomposite samples of UV-Vis results as below (Figure 4.26). From the figure, it was understood that the UV absorption behavior of PBZE1-EPDM-PTFE-Nano $TiO_2$ polymer nanocomposites is increased with adding sulfur and increasing vulcanization temperature of polymer nanocomposite. Regarding UV graphs, we acquired more absorption from PBZE1-EPDM-PTFE-Nano $TiO_2$ polymer nanocomposite sample with sulfur, vulcanized at 150 °C (Figure 4.26 (d)).
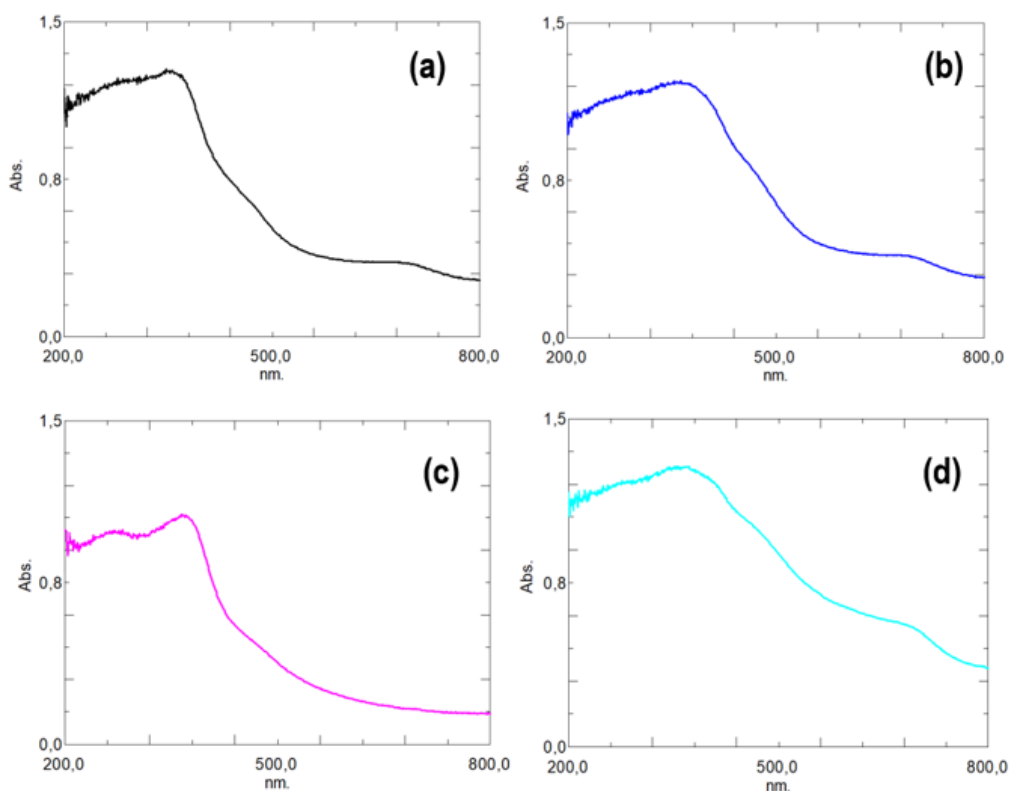


**Figure 4.26.** The results of UV-Vis. analysis for PBZE1-EPDM-PTFE-Nano $TiO_2$ polymer nanocomposite samples. a) PBZE1-EPDM-PTFE-Nano $TiO_2$, b) PBZE1-EPDM-PTFE-Nano $TiO_2$-150, c) PBZE1-EPDM-PTFE-Nano $TiO_2$-S, d) PBZE1-EPDM-PTFE-Nano $TiO_2$-S-150

The UV-Vis. analysis results for other PBZE1-EPDM-PTFE-Nano $TiO_2$ polymer nanocomposite samples as shown in below. (Figure 4.27 – Figure 4.32)
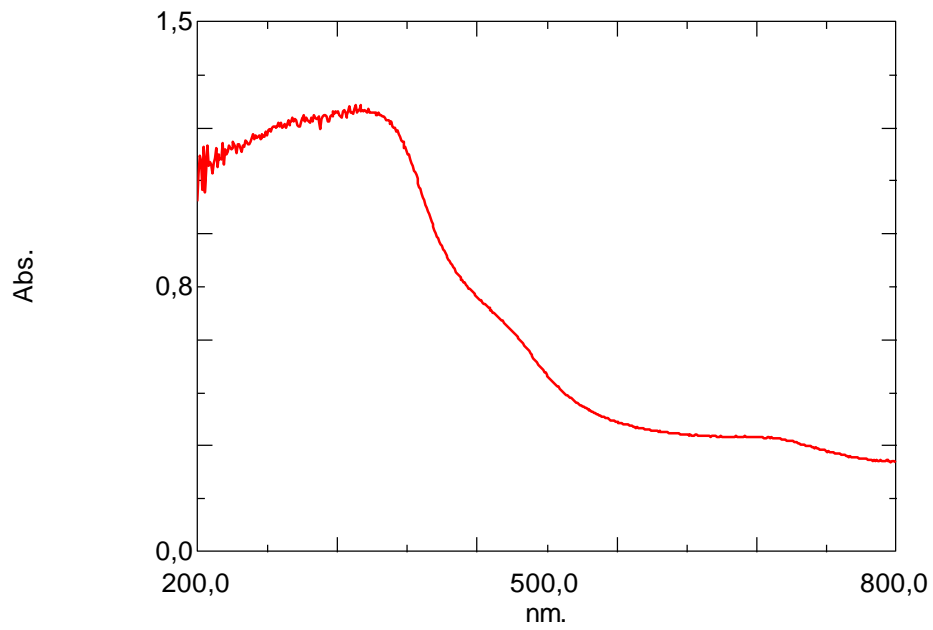
**Figure 4.27.** The UV-vis analyze for PBZE1-EPDM-PTFE-Nano TiO$_2$-100 polymer nanocomposite sample
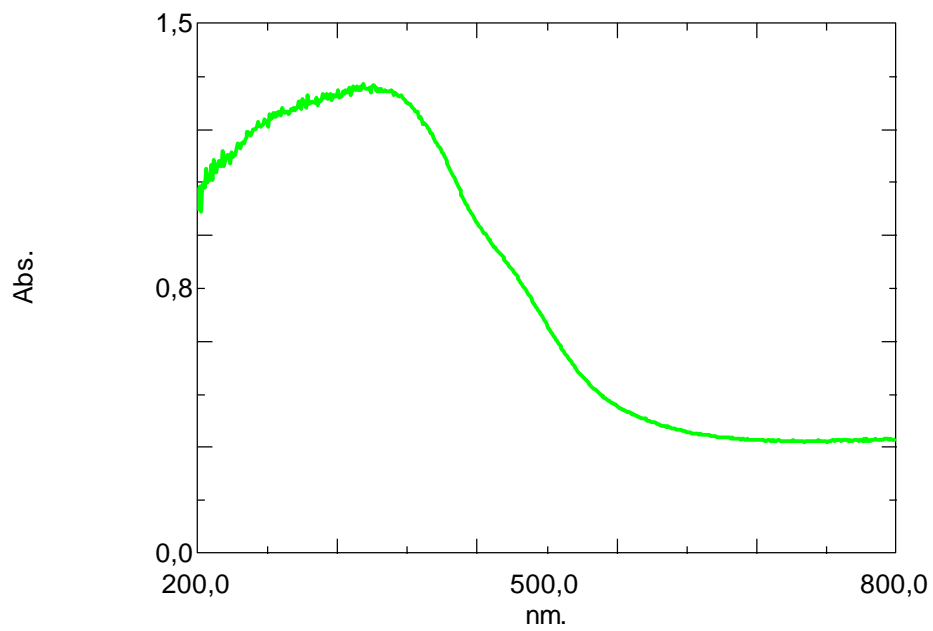


**Figure 4.28.** The UV-vis analyze for PBZE1-EPDM-PTFE-Nano TiO$_2$-180 polymer nanocomposite sample
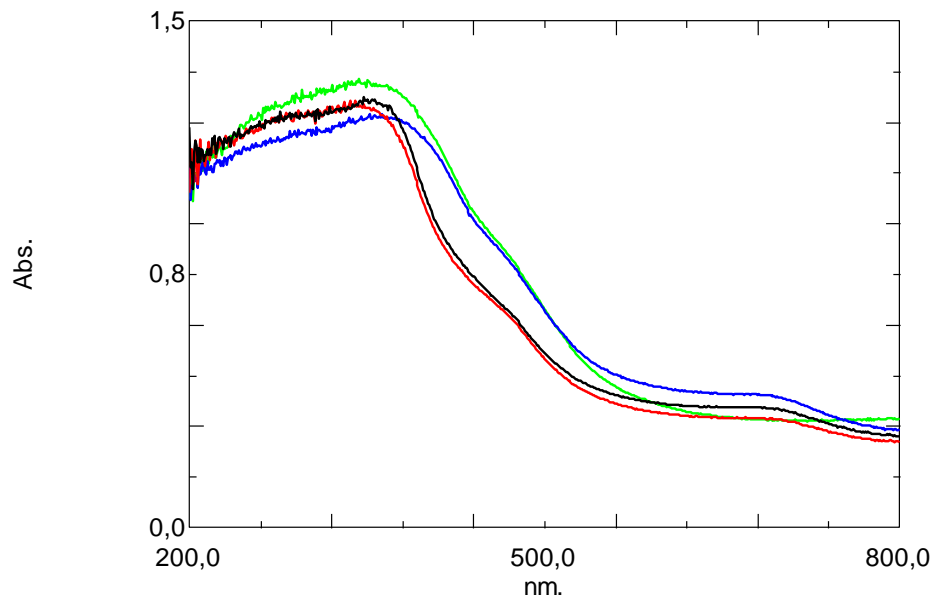
**Figure 4.29.** The compare of UV-vis. analysis for PBZE1-EPDM-PTFE-Nano TiO$_2$ nanocomposite samples without sulfur
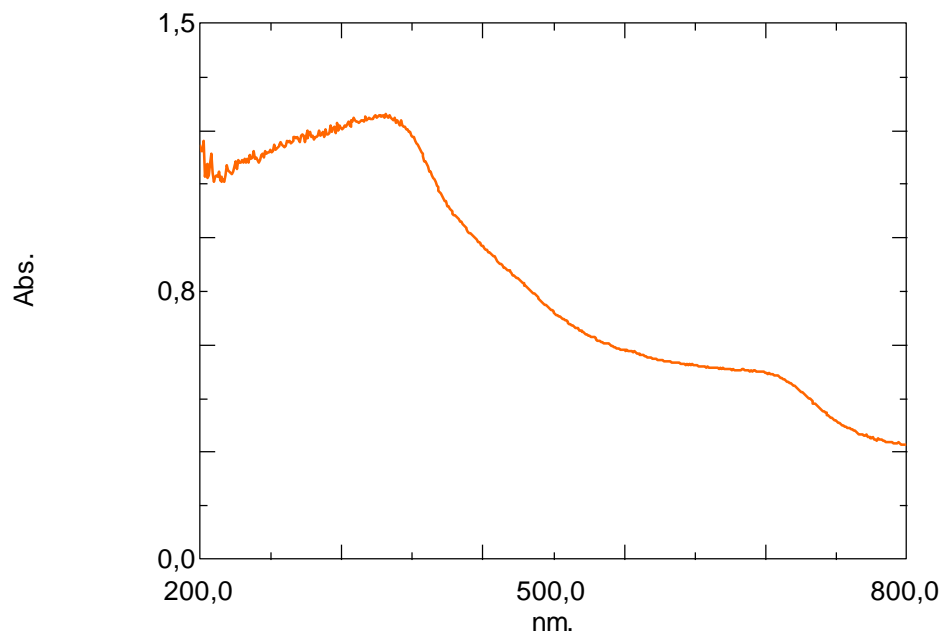


**Figure 4.30.** The UV-vis analyze for PBZE1-EPDM-PTFE-Nano TiO$_2$-S-100 polymer nanocomposite sample
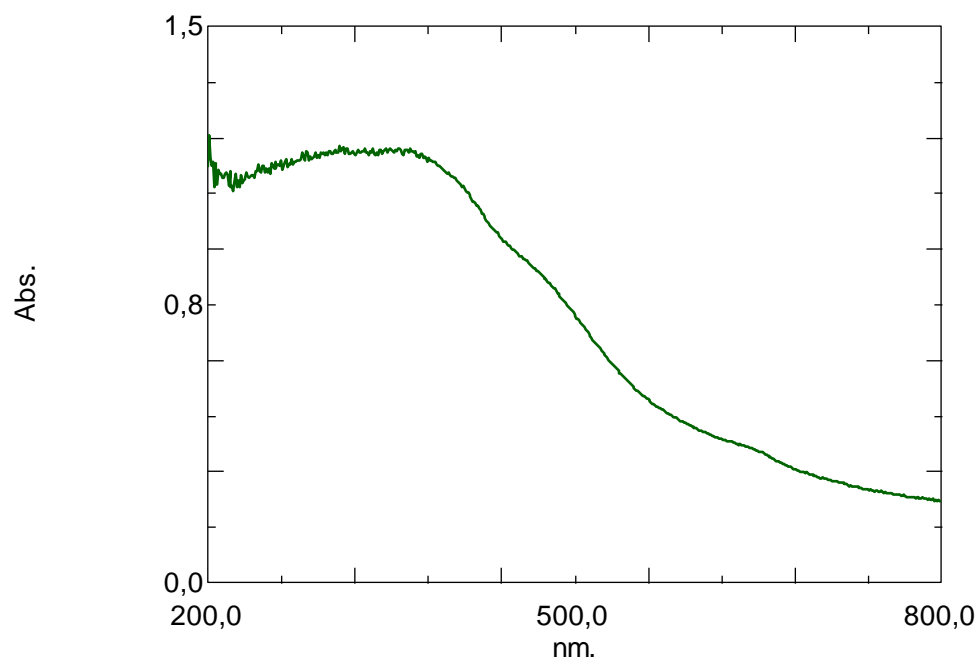
**Figure 4.31.** The UV-vis analyze for PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer nanocomposite sample
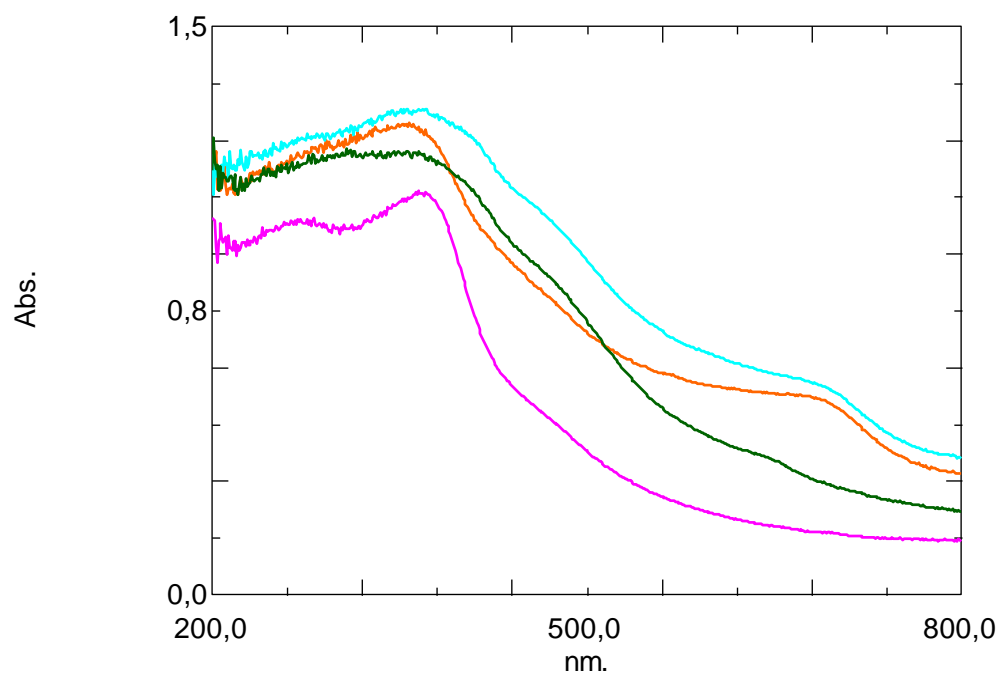


**Figure 4.32.** The compare of UV-vis. analysis for PBZE1-EPDM-PTFE-Nano TiO$_2$ nanocomposite samples with sulfur

Fourier-transform infrared (FTIR) spectra of KBr disks were obtained using a Perkin Elmer FT IR Spectrometer Spectrum Two. The FTIR spectra of PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite samples prepared at different temperature with and without sulfur are recorded in the wave number range of 400–4000 cm$^{-1}$ (Figure 4.33 and Figure 4.34). In the Figure 4.33, the peaks appeared at 2920 cm$^{-1}$ and 2851

cm$^{-1}$ were conforming to C–H aliphatic stretch vibration and alkyl side chain of PBZ [200]. The peak appeared at 1461 cm$^{-1}$ is due to the benzene ring of benzoxazine and the peak appeared at 1599 cm$^{-1}$ was represented for aromatic C – N stretching. The IR spectra show symmetric peaks characteristic of Ti – O – Ti (720–504 cm$^{-1}$) [202,203].
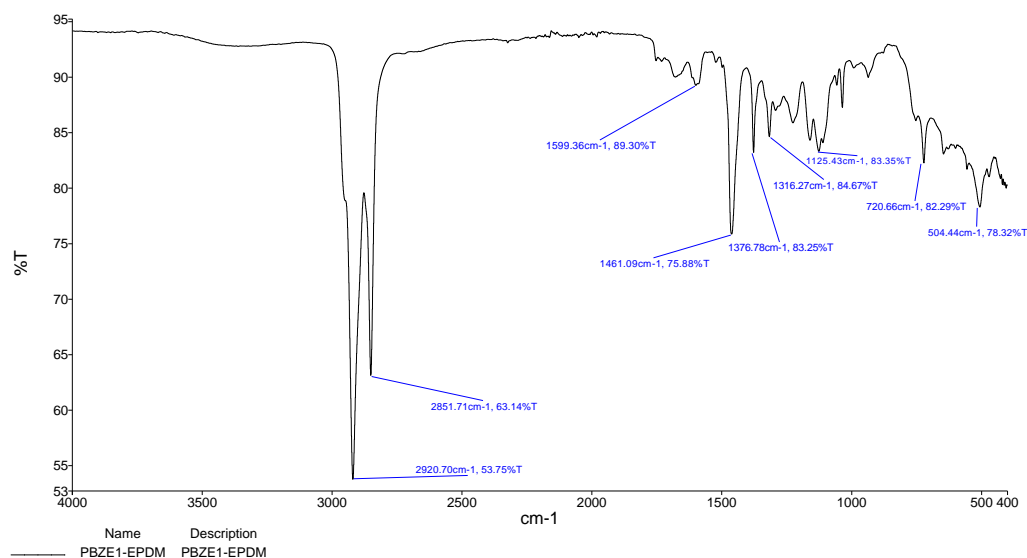


**Figure 4.33.** The FTIR spectrum of PBZE1-EPDM

The effect of sulfur and vulcanization temperature at 150 °C induced low transmittance values as shown in Figure 4.34. It can be seen similar peak with Figure 4.32 at 2922 cm$^{-1}$ was represented stretching vibration of aliphatic C – H. Also, the peak appeared at 1455 cm$^{-1}$ is due to the benzene ring of benzoxazine and the peak appeared at 1587 cm$^{-1}$ was represented for aromatic C-N stretching similar with first spectrum. The O–H stretching is giving the idea at 3400–3500 cm$^{-1}$ as a broad peak. The PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite sample with sulfur after vulcanization, the O- . . ..H+N intramolecular hydrogen bonding was observed at 2852 cm$^{-1}$ and OH. . ..O intermolecular hydrogen bonding was monitored around 3400 cm$^{-1}$ [204,205,206]. In the low-energy interval, the intensity and symmetry of the absorption peaks of the spectra in Figure 4.34 more than Figure 4.33. The new peaks were observed in Figure 4.34 at 1102 cm$^{-1}$ and 1033 cm$^{-1}$. Regarding these results of FTIR spectrum in Figure 4.34 it may be sayable; the vulcanization of EPDM with sulfur and thermal treatment of the PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite was succeeded to prepare the hydrophobic polymer nanocomposite.
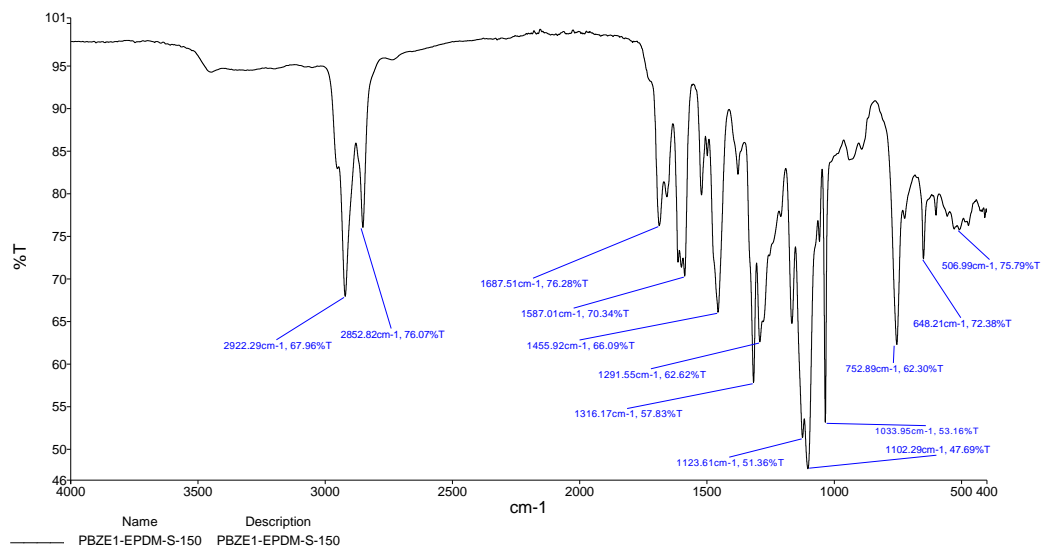
**Figure 4.34.** The FTIR spectrum of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-150

Other FTIR spectra for all of PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer nanocomposite samples like below. (Figure 4.35 – Figure 4.44)
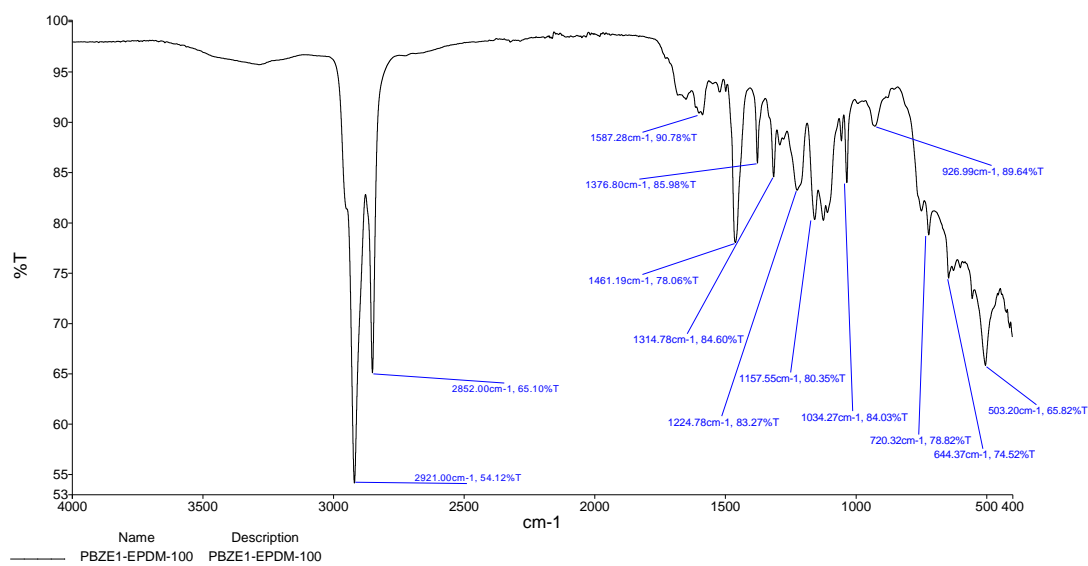


**Figure 4.35.** The FTIR spectrum of PBZE1-EPDM-PTFE-Nano TiO$_2$-100
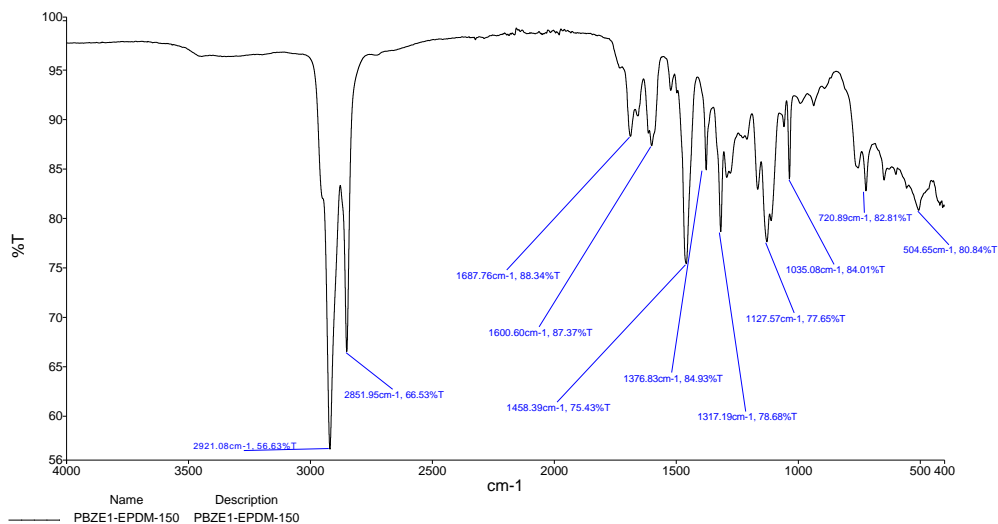
**Figure 4.36.** The FTIR spectrum of PBZE1-EPDM-PTFE-Nano TiO$_2$-150
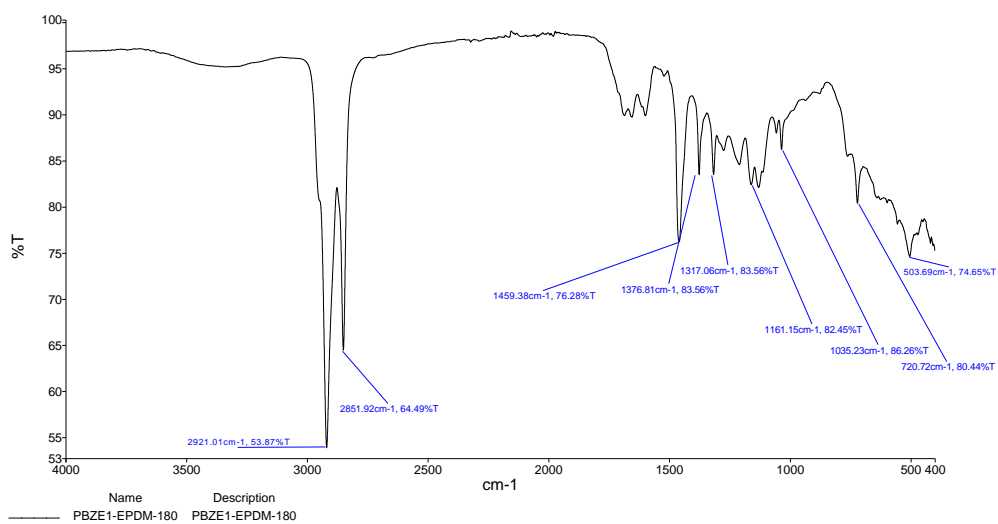


**Figure 4.37.** The FTIR spectrum of PBZE1-EPDM-PTFE-Nano TiO$_2$-180
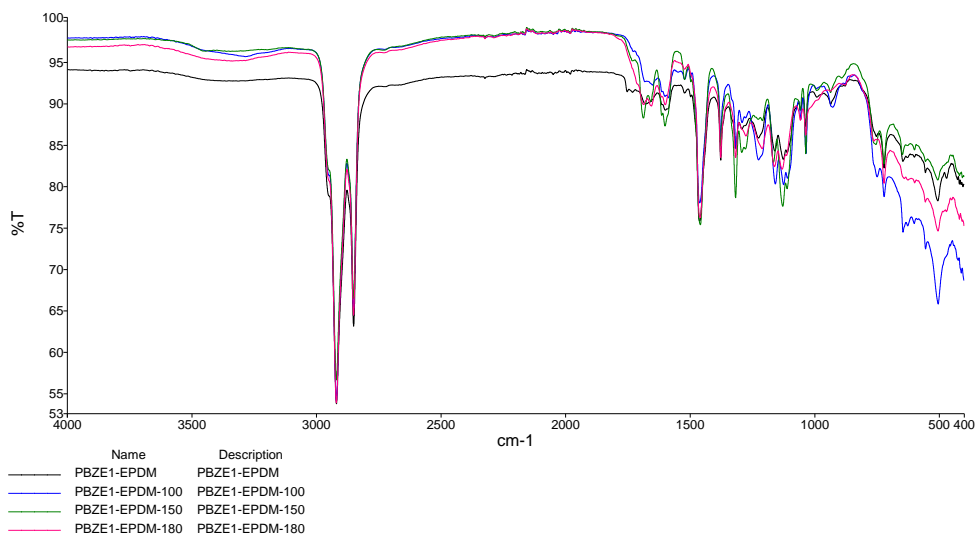
**Figure 4.38.** The compare of FTIR spectra for the PBZE1-EPDM-PTFE-Nano TiO$_2$ nanocomposite samples without sulfur
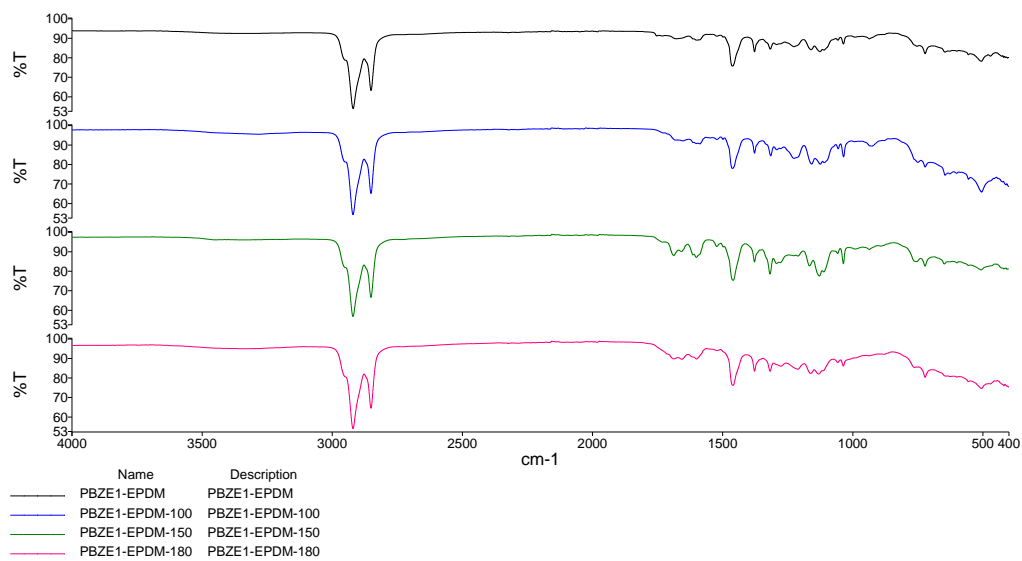


**Figure 4.39.** The compare of FTIR spectra for the PBZE1-EPDM-PTFE-Nano TiO$_2$ nanocomposite samples without sulfur
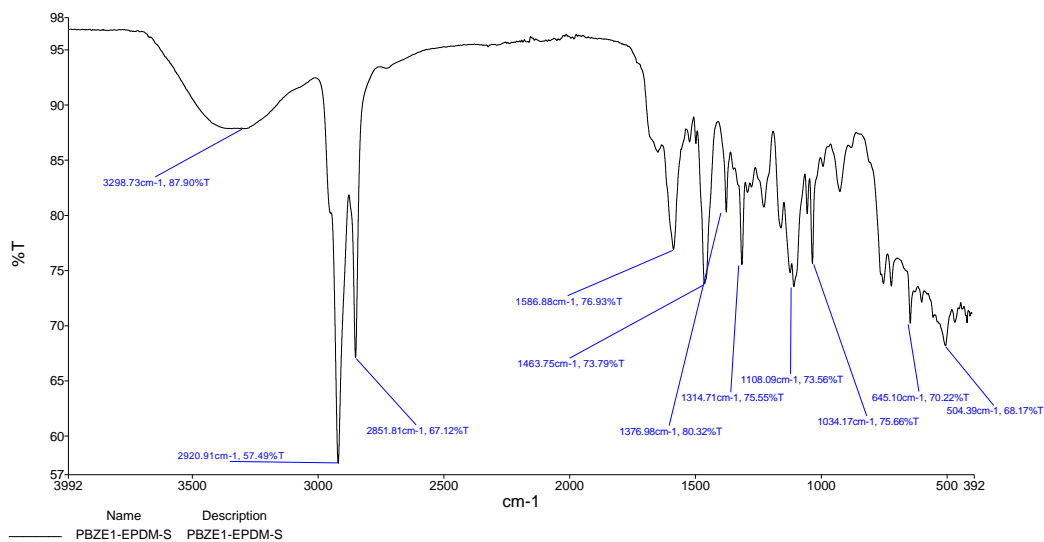
**Figure 4.40.** The FTIR spectrum of PBZE1-EPDM-PTFE-Nano TiO$_2$-S
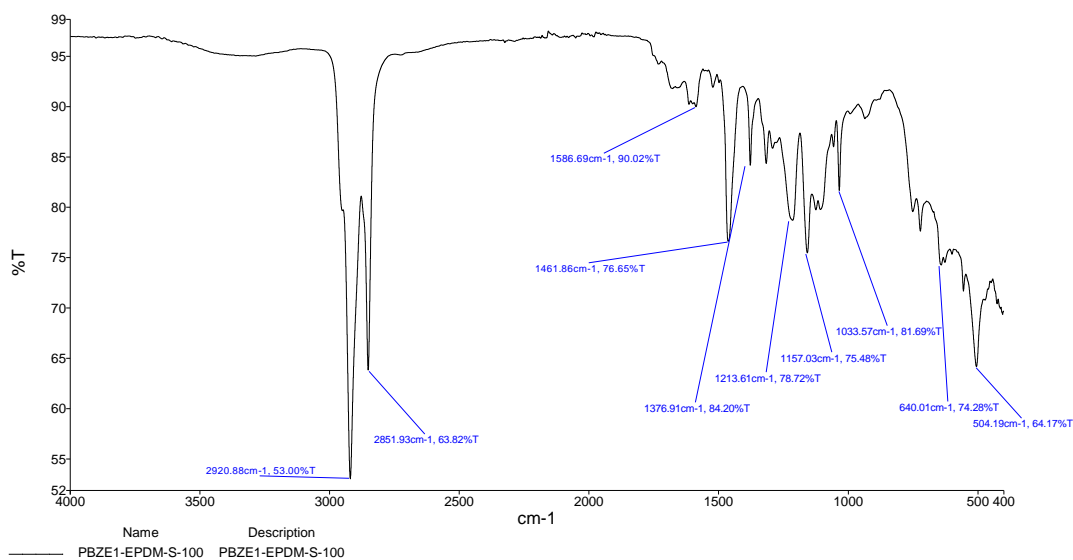


**Figure 4.41.** The FTIR spectrum of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-100
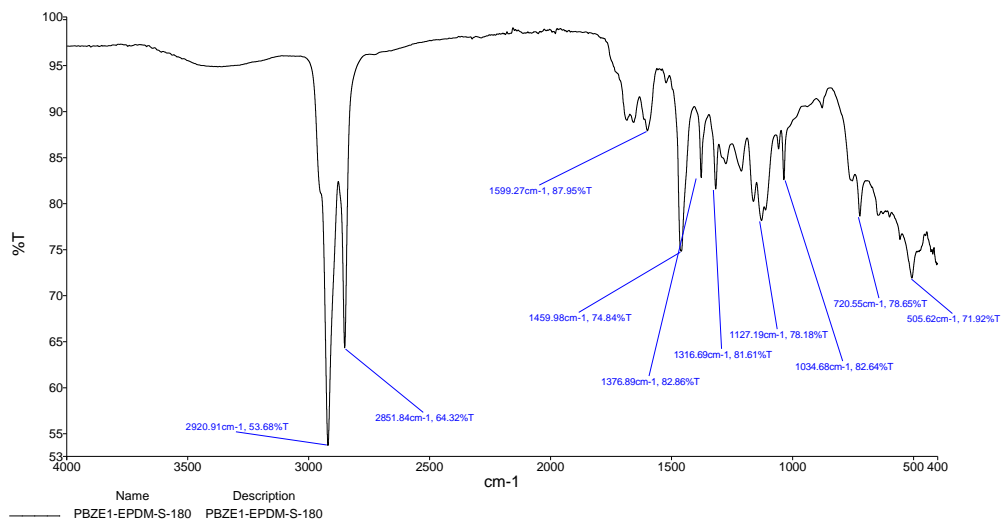
**Figure 4.42.** The FTIR spectrum of PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180
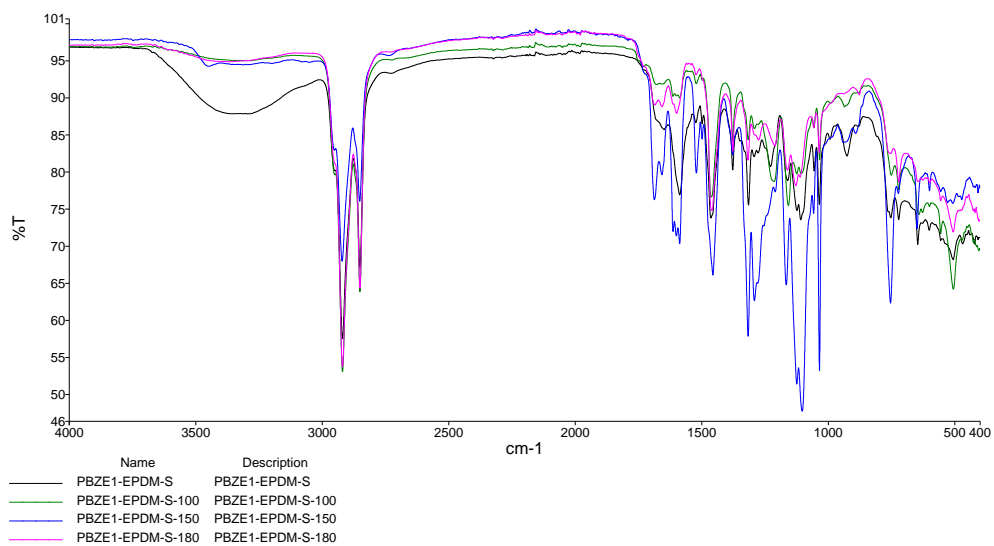


**Figure 4.43.** The compare of FTIR spectra for the PBZE1-EPDM-PTFE-Nano TiO$_2$ nanocomposite samples with sulfur
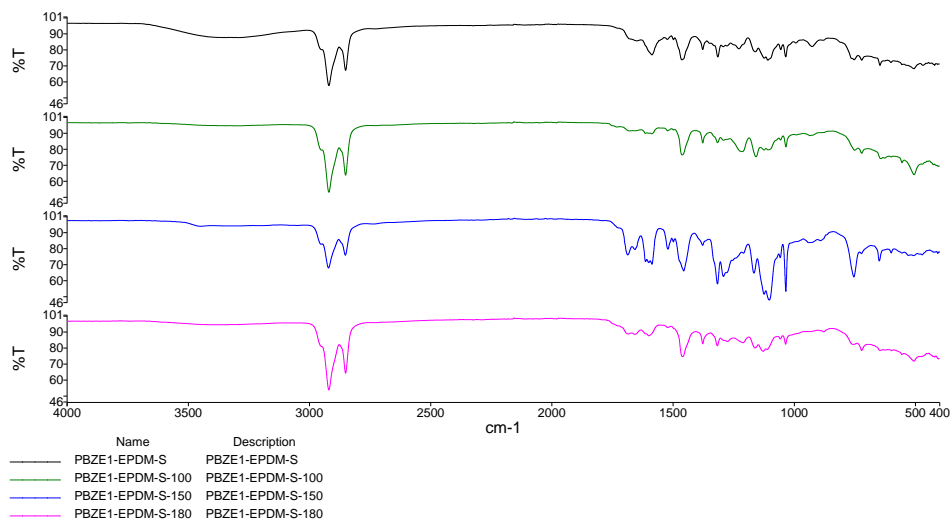
**Figure 4.44.** The compare of FTIR spectra for the PBZE1-EPDM-PTFE-Nano TiO$_2$ nanocomposite samples with sulfur

NETZSCH STA 449F1 brand thermogravimetric analysis (TGA) device was used for the thermal analysis of the mixtures. The samples were prepared at 10 °C/min. from room temperature to 800 °C according to ASTM D6370 standard. % mass loss was analyzed by testing in nitrogen environment with temperature increase. The TG-DTA curves of the samples are given below. (Figure 4.45 – Figure 4.50)
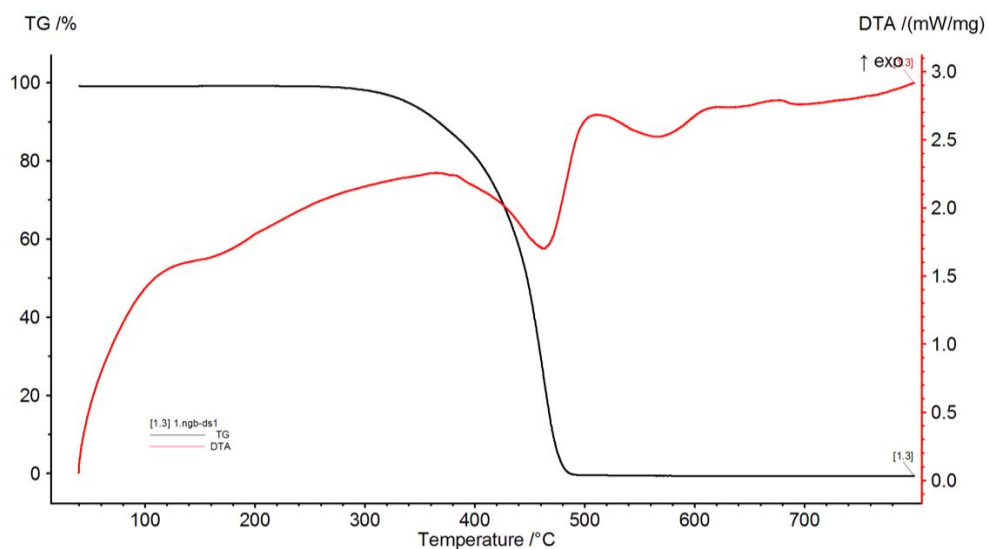


**Figure 4.45.** TGA-DTA curve for PBZE1 polymer
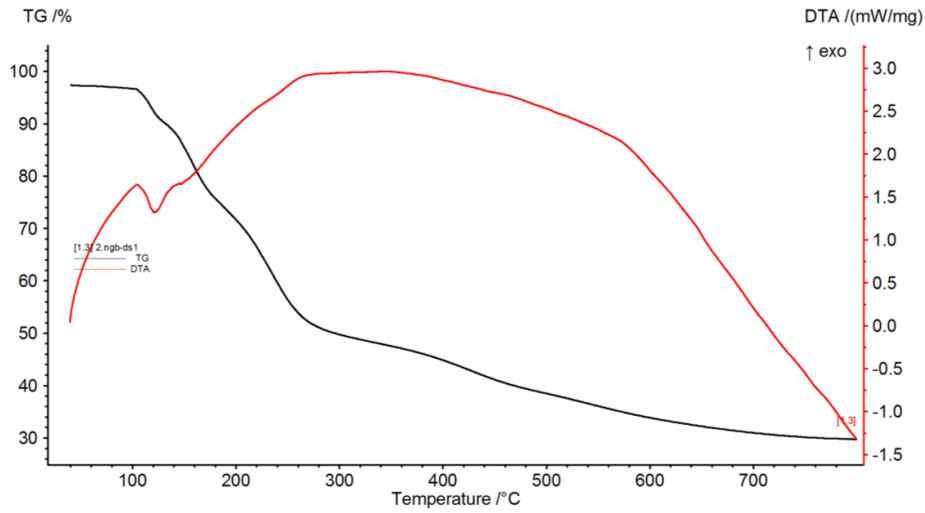
**Figure 4.46.** TGA-DTA curve for EPDM rubber
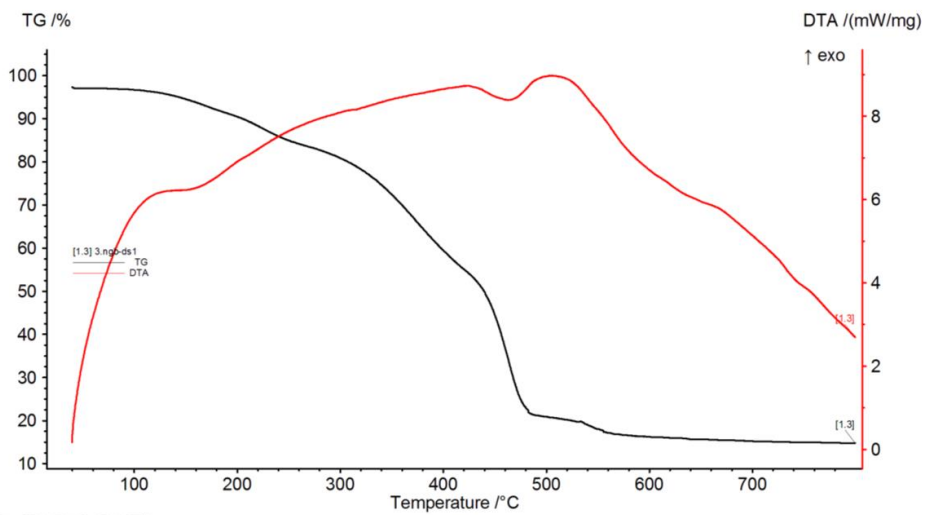


**Figure 4.47.** TGA-DTA curve for PBZE1-EPDM-PTFE-Nano TiO$_2$-S polymer nanocomposite sample
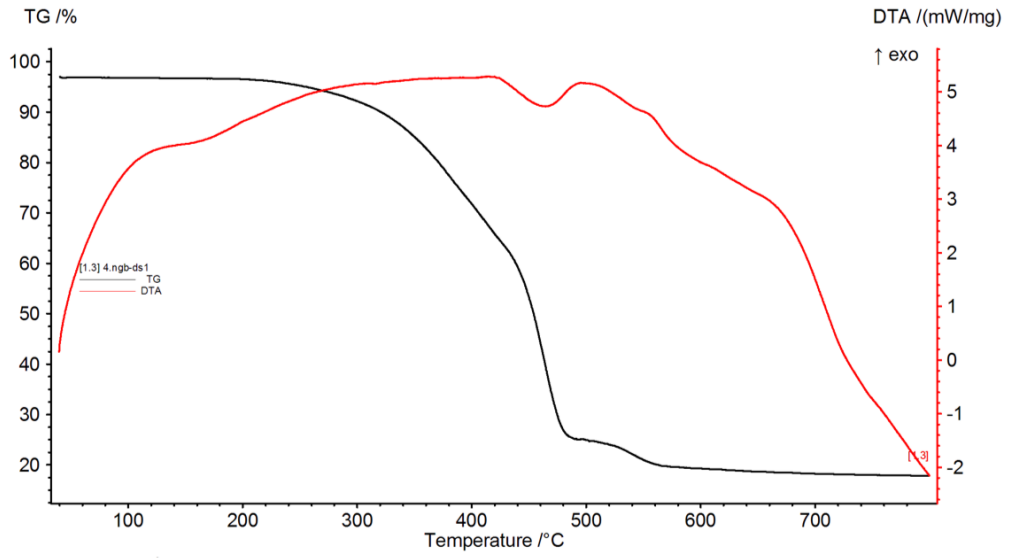
**Figure 4.48.** TGA-DTA curve for PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 polymer
nanocomposite sample
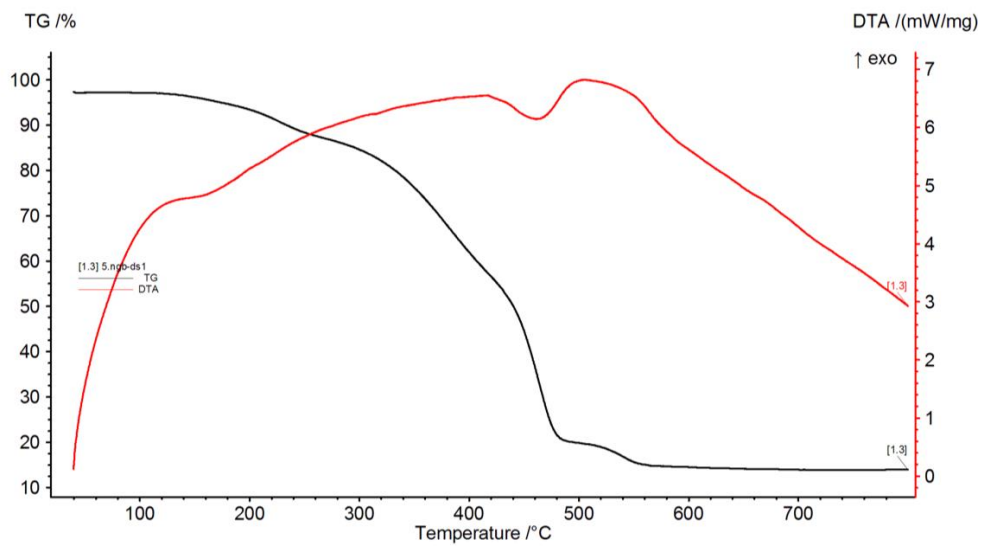


**Figure 4.49.** TGA-DTA curve for PBZE1-EPDM-PTFE-Nano TiO$_2$ polymer
nanocomposite sample
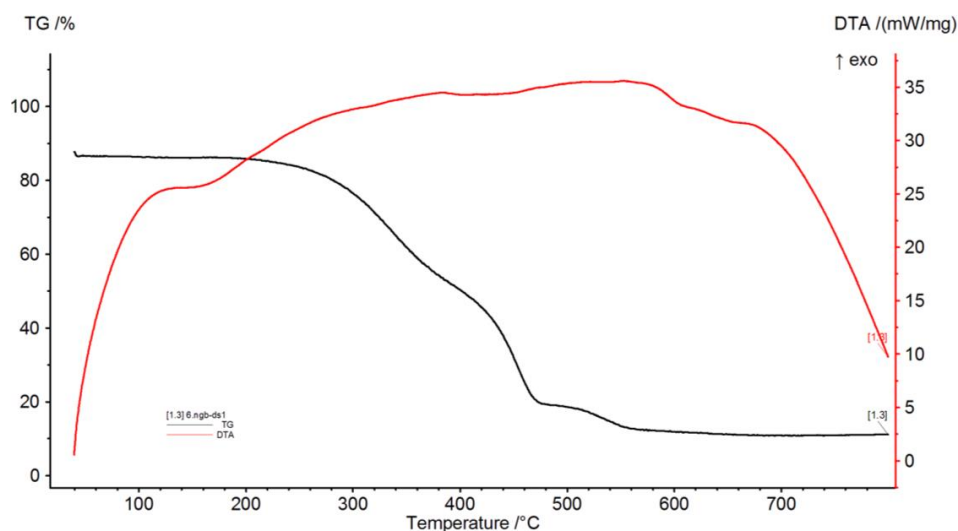
**Figure 4.50.** TGA-DTA curve for PBZE1-EPDM-PTFE-Nano TiO$_2$-180 polymer nanocomposite sample

Results of TGA-DTA curves for samples are given in the Table 4.5. T$_{d5}$ is the decomposition temperature at 5% mass loss, T$_{d10}$ is the decomposition temperature at 10% mass loss and T$_{max}$ is the decomposition temperature at maximum mass loss.

**Table 4.5.** Results of TGA-DTA curves for samples

| Sample Name | T$_{d5}$ (°C) | T$_{d10}$ (°C) | T$_{max}$ (°C) | Ash content (%) |
|---|---|---|---|---|
| PBZE1 | 337,5 | 367,3 | 486,6 | 24,08 |
| EPDM | 111,6 | 131,5 | - | 25,53 |
| PBZE1-EPDM-PTFE-Nano TiO$_2$-S | 143,8 | 203,4 | - | 7,35 |
| PBZE1-EPDM-PTFE-Nano TiO$_2$-S-180 | 255,6 | 320,2 | - | 10,60 |
| PBZE1-EPDM-PTFE-Nano TiO$_2$ | 173,74 | 233,3 | - | 9,01 |
| PBZE1-EPDM-PTFE-Nano TiO$_2$-180 | - | - | - | 1,93 |

## 5. CONCLUSION

In this study, polybenzoxazine and ethylene propylene diene monomer rubber polymer nanocomposite filled by 0-20 nanometer titanium dioxide and polytetrafluoroethylene have been prepared. We have investigated the effects of sulfur and different vulcanization temperatures on surface structure, hydrophobicity, chemical, thermal and optical properties of polymer nanocomposites.

- SEM images showed that EPDM and PBZ polymer phases were homogenously mixed in blends.

- SEM images showed the filler dispersion was done homogeneously and it was achieved to prepare hydrophobic EPDM-PBZ polymer nanocomposite.

- SEM-EDX results showed effect of applied temperature and vulcanization process.

- According to the contact angle measurements, it was confirmed that including sulfur to polymer nanocomposite at 180 °C vulcanization temperature has the lowest surface free energy and highest contact angle of 110° than other samples.

- In the UV-vis analysis, it was observed wide range, broad peaks. It's important for understanding crosslinking density of the sample. The best result came from PBZE1-EPDM-PTFE-Nano $TiO_2$-S-150 polymer nanocomposite sample.

- The FTIR spectra present the intensity of the absorption peaks of the polymer nanocomposite with sulfur vulcanized at 150 °C more than other nanocomposite samples.

- TGA-DTA analysis results showed improved thermal properties using fillers and PBZ blending. It was observed, the PBZE1 polymer may be degrade at very high temperature. After prepared a blend with PBZE1 and EPDM rubber, the degradation temperature a bid decreased because of low degradation temperature of EPDM rubber.

To prepare hydrophobic polymer nanocomposite, it was chosen hydrophobic materials within every step of process. First, to synthesize hydrophobic PBZ, it was chosen 2-(Trifluoromethyl)aniline. Owing to Fluorine in the aniline, the PBZ resin didn't solve within the water. So, it was obtained hydrophobic PBZ resin. Second, to support hydrophobic and mechanical properties of PBZ resin, it was chosen EPDM rubber. EPDM rubber gave the elasticity and toughness in addition with hydrophobic property to polymer nanocomposites. And third, the additive materials were chosen hydrophobic materials such as nano $TiO_2$ and PTFE. All of these selections, was help to prepare hydrophobic nanocomposite.

Regarding to the test results, the PBZE1-EPDM-PTFE-Nano $TiO_2$ polymer nanocomposite sample with sulfur, vulcanized over 150 °C displayed better hydrophobic surface properties.

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